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(54) **PREPARATION OF ZEOLITES USING ORGANIC TEMPLATE AND AMINE**

HERSTELLUNG VON ZEOLITHEN UNTER VERWENDUNG VON ORGANISCHEM TEMPLAT UND AMIN

PREPARATION DE ZEOLITHES A L'AIDE D'UNE MATRICE ORGANIQUE ET D'AMINE

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Description

[0001] Natural and synthetic zeolitic crystalline aluminosilicates are useful as catalysts and adsorbents. These aluminosilicates have distinct crystal structures which are demonstrated by X-ray diffraction. The crystal structure defines cavities and pores which are characteristic of the different species. The adsorptive and catalytic properties of each crystalline aluminosilicate are determined in part by the dimensions of its pores and cavities. Thus, the utility of a particular zeolite in a particular application depends at least partly on its crystal structure.

[0002] Because of their unique molecular sieving characteristics, as well as their catalytic properties, crystalline aluminosilicates are especially useful in such applications as gas drying and separation and hydrocarbon conversion. Although many different crystalline aluminosilicates and silicates have been disclosed, there is a continuing need for new zeolites and silicates with desirable properties for gas separation and drying, hydrocarbon and chemical conversions, and other applications.

[0003] Crystalline aluminosilicates are usually prepared from aqueous reaction mixtures containing alkali or alkaline earth metal oxides, silica, and alumina. "Nitrogenous zeolites" have been prepared from reaction mixtures containing an organic templating agent, usually a nitrogen-containing organic cation. Use of adamantane materials as the templates for making molecular sieves, particularly zeolites, is disclosed in U.S. Patent No. 4,665,110, issued May 12, 1987 to Zones which is hereby incorporated by reference. Adamantane materials are used as the templates in making a particular zeolite, SSZ-25, as disclosed in U.S. Patent No. 4,826,667, issued May 2, 1989 to Zones et al., and pending application No. 788,656 filed November 6, 1991, which is a continuation of U.S. Serial No. 333,666 filed April 5, 1989, both of which are hereby incorporated by reference. Use of hexamethyleneimine as the sole template in making zeolites similar to SSZ-25 is disclosed in U.S. Patents No. 4,439,409, issued March 27, 1984 to Puppe et al., and 4,954,325, issued September 4, 1990 to Rubin et al., while use of hexamethyleneimine and piperidine as the template in making a zeolite similar to SSZ-25 is disclosed in European Patent Application No. 0,293,032 A2, dated May 11, 1988. Use of adamantanamine materials in making a zeolite other than SSZ-25 is disclosed in U.K. Pat. Application GB 2,193,202 A, dated February 3, 1988. Another zeolite utilizing amines in its manufacture is the intermediate pore-size zeolite ZSM-5. U.S. Patent No. 4,495,166, issued January 22, 1985 to Calvert et al., discloses use of a small amount of a quaternary ammonium compound such as tetrapropyl ammonium in conjunction with other amines to make ZSM-5.

[0004] U.S. Patent No. 5,057,296, issued October 15, 1991 to Beck, discloses a process for producing ultra-large pore (sometimes called "mesoporous") crystalline materials using a two component system containing an organic template and an amine. These mesoporous materials have uniformly sized pores with a maximum perpendicular cross section of at least about 13 Å. The second component of the system (the amine) is used to expand the pore size of these materials to the required 13 Å or greater size by expanding the micelle created to form these mesoporous materials.

[0005] The mesoporous materials of the Beck patent are considered very different from microporous materials, such as zeolites, and are not currently considered to be zeolites.

SUMMARY OF THE INVENTION

[0006] Crystalline, microporous aluminosilicate molecular sieves have been prepared in accordance with this invention using a highly effective new method.

[0007] In accordance with this invention there is provided a method for preparing a zeolite selected from the group consisting of large pore zeolites, medium pore zeolites having unidimensional channels, and small pore zeolites, said method comprising:

A. forming an aqueous reaction mixture comprising (1) a source of an oxide selected from silicon oxide, germanium oxide and mixtures thereof; (2) a source of an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide and mixtures thereof; (3) a source of an alkali metal oxide; (4) an amine component comprising at least one amine containing one to eight carbon atoms, ammonium hydroxide, and mixtures thereof, and (5) an organic templating compound capable of forming said zeolite in the presence of said amine, wherein said amine is smaller than said organic templating compound; and

B. maintaining said aqueous mixture under sufficient crystallization conditions until crystals are formed.

[0008] There is further provided in accordance with this invention an improved method for preparing a zeolite selected from the group consisting of large pore zeolites, medium pore zeolites having unidimensional channels, and small pore zeolites from source materials for said zeolite and an organic templating compound, the improvement comprising employing a mixture of (1) said organic templating compound, and (2) an amine component comprising at least one

amine containing one to eight carbon atoms, ammonium hydroxide, and mixtures thereof, said amine being smaller than said organic templating compound and said organic templating compound being capable of forming said zeolite in the presence of said amine.

[0009] The present invention also provides these processes wherein the organic templating compound is selected from the group consisting of quaternary ammonium ions, cyclic amines and polar adamantyl derivatives.

[0010] In a preferred embodiment, the present invention provides these processes wherein the organic templating compound is used in an amount less than that required to fill all of the micropore volume of the zeolite.

[0011] In accordance with this invention, there is also provided a zeolite having an as-synthesized molar composition in an anhydrous state of $(0.02 \text{ to } 2.0)Q:(0.02 \text{ to } 1.0)Z:(0.1 \text{ to } 2.0)M_2O:W_2O_3:(10 \text{ to } 200)YO_2$, wherein M is an alkali metal cation; W is selected from aluminum, gallium, iron, boron, titanium and mixtures thereof; Y is selected from silicon, germanium, and mixtures thereof; Z is an amine component comprising at least one amine containing from one to eight carbon atoms, ammonium hydroxide, and mixtures thereof; and Q is an organic templating compound capable of forming the zeolite in the presence of the amine.

[0012] Among other factors, the present invention is based on the discovery that amines which could be used in the synthesis of small and medium pore-sized zeolites can be used to synthesize the large-pore zeolites, such as the zeolite known as "Zeolite SSZ-25" or simply "SSZ-25", when used in conjunction with a small amount of an organic templating compound, such as an adamantane compound for SSZ-25. For example, ZSM-5, a medium pore size, multidimensional zeolite, was produced when the amine piperidine or cyclopentylamine was used alone (see Table 4, Examples 7 and 9) as the templating compound. However, when a small amount of an adamantyl quaternary ammonium ion was used in combination with piperidine or cyclopentylamine, the large-pore zeolite SSZ-25 resulted (see Table 4, Examples 6 and 8). This is particularly surprising since the amount of the adamantyl quaternary ammonium ion that was used was insufficient to cause significant growth of SSZ-25 if used without other amines present.

[0013] It was wholly unexpected that amines such as isobutyl, neopentyl, or monomethyl amine could be used in relatively large quantities to produce zeolites such as SSZ-25 (see Table 3, Examples 3 and 4). Use of amines containing from one to eight carbon atoms provides significant cost savings over the method of using, e.g., an adamantyl quaternary ammonium ion as the sole source of organic component. Additional manufacturing flexibility can be obtained, since the process no longer depends on the availability of large quantities of one particular amine.

[0014] In addition to these discoveries, it was found that polar adamantyl derivatives could be substituted for the more costly adamantyl quaternary ammonium ions being used in combination with the amine component to prepare SSZ-25 (see Examples 4, 5, 11, and 12), even though these polar adamantyl derivatives do not result in crystallization of SSZ-25 when used alone. Therefore, the cost of making SSZ-25 is further reduced.

[0015] Substantial reductions in growth time also occurred unexpectedly when using the organic component mixture comprising an amine component and an organic templating compound. Growth times improved by a factor of from approximately two to approximately five in some examples. The commercial benefits of reduced plant construction cost for a given production rate will be substantial.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0016] The zeolites prepared in accordance with this invention are microporous, crystalline materials which have a mole ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide and mixtures thereof in the range of 10 to 200. These zeolites further have a composition, as synthesized and in the anhydrous state, in terms of mole ratios as follows: $(0.02 \text{ to } 2.0)Q:(0.02 \text{ to } 1.0)Z:(0.1 \text{ to } 2.0)M_2O:W_2O_3:(10 \text{ to } 200)YO_2$, wherein M is an alkali metal cation; W is selected from aluminum, gallium, iron, boron, titanium and mixtures thereof; Y is selected from silicon, germanium, and mixtures thereof; Z is an amine component comprising at least one amine containing from one to eight carbon atoms, ammonium hydroxide, and mixtures thereof; and Q is an organic templating agent capable of forming the zeolite in the presence of the amine.

[0017] The present invention involves a novel method for preparing zeolites, comprising the preparation of an aqueous mixture that contains sources of a minor quantity of an organic templating compound capable of forming the desired zeolite, a larger quantity of an amine component containing at least one small amine ranging from 1 to 8 carbons, and/or ammonium hydroxide, and preferably seeds of the desired zeolite. Preferably, the amine component is an aliphatic or cycloaliphatic amine containing no more than 8 carbon atoms or mixtures of such compounds.

[0018] This invention provides considerable cost improvement and flexibility in choice of organic components, and most surprisingly, faster crystallization rates.

[0019] The present invention is useful in preparing large pore zeolites having unidimensional channels, large pore zeolites having multidimensional channels, medium pore zeolites having unidimensional channels, small pore zeolites having unidimensional channels and small pore zeolites having multidimensional channels. As used herein, the term "large pore zeolite" refers to zeolites which have ≥ 12 -ring openings in their framework structure, the term "medium

pore zeolites" refers to zeolites which have 10-ring openings in their framework structure, and the term "small pore zeolites" refers to zeolites which have ≤ 8 -ring openings in their framework structure. In addition, the term "unidimensional" or "unidimensional channels" refers to the fact that the pores in the zeolite form channels which are essentially parallel and do not intersect, and the term "multidimensional" or "multidimensional channels" refers to the fact that the pores in the zeolite form channels which do intersect each other.

[0020] The reaction mixtures used to prepare the zeolites by the method of this invention may have a composition, in terms of mole ratios, falling within the following ranges: $\text{YO}_2:\text{W}_2\text{O}_3$, 10:1 to 200:1; $\text{M}:\text{YO}_2$ 0.01:1 to 0.50:1; $\text{OH}:\text{YO}_2$ 0.01:1 to 0.60:1; $\text{Q}:\text{YO}_2$ 0.02:1 to 1.00:1 and $\text{Z}:\text{YO}_2$ 0.02:1 to 1.00:1, where Y is selected from silicon, germanium, and mixtures thereof; W is selected from aluminum, gallium, iron, boron, titanium and mixtures thereof; M is an alkali metal cation; Z is an amine component comprising at least one amine containing from one to eight carbon atoms, ammonium hydroxide, or mixtures thereof; and Q is an organic templating compound capable of forming the zeolite in the presence of the amine.

[0021] In some instances, the alkali metal cation level in the reaction mixture should be carefully controlled. It has now been discovered that alkali metal cation: SiO_2 mole ratios much above 0.40 can favor the formation of the zeolites ZSM-5 and mordenite. Indeed, it has been found that at high alkali metal cation: SiO_2 mole ratios, these two zeolites can be produced even in the absence of any organic templating compound. Thus, in order to ensure that the desired zeolite is produced, it is advisable to carefully control the alkali metal cation content in the reaction mixture. To this end, it may also be advisable to avoid using reagents such as sodium and potassium silicates.

[0022] The present invention will now be described with respect to one of the zeolites, SSZ-25, which can be made using the method of this invention. It is understood that the other zeolites which can be made using this method are made in substantially the same way.

[0023] SSZ-25 has a mole ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide and mixtures thereof in the range of 10 to 200, and having the X-ray diffraction lines of Table 2 below. The zeolite further has a composition, as synthesized and in the anhydrous state, in terms of mole ratios of oxides as follows: $(0.02 \text{ to } 2.0)\text{Q}:(0.20 \text{ to } 1.0)\text{Z}:(0.1 \text{ to } 2.0)\text{M}_2\text{O}:\text{W}_2\text{O}_3:(10 \text{ to } 200)\text{YO}_2$, wherein M is an alkali metal cation; W is selected from aluminum, gallium, iron, boron, titanium and mixtures thereof; Y is selected from silicon, germanium, and mixtures thereof; and Q is an adamantane compound comprising at least one compound chosen from the group consisting of adamantane quaternary ammonium ions and polar adamantyl derivatives, and Z is an amine component comprising at least one amine chosen from amines containing from one to eight carbon atoms. SSZ-25 zeolites can have a $\text{YO}_2:\text{W}_2\text{O}_3$ mole ratio in the range of about 10 to 200. As prepared, the silica to alumina mole ratio is typically in the range of about 15:1 to about 100:1. Higher mole ratios can be obtained by treating the zeolite with chelating agents or acids to extract aluminum from the zeolite lattice. The silica to alumina mole ratio can also be increased by using silicon and carbon halides and other similar compounds. Preferably, SSZ-25 is an aluminosilicate wherein W is aluminum and Y is silicon.

[0024] SSZ-25 zeolites, as synthesized in the presence of adamantyl compounds, have crystalline structures with the X-ray powder diffraction patterns containing the following characteristic lines:

TABLE 1(a)

2 θ	d/n	Int.
5.0	17.7	2 Br
6.92	12.77	28
7.06	12.52	26
7.87	11.23	21
8.78	10.07	1
9.31	9.5	5
9.93	8.91	42
12.47	7.10	2
12.79	6.92	7
14.00	6.33	22
14.21	6.23	24
14.67	6.04	10
15.87	5.58	15
17.65	5.02	2
18.89	4.70	5
20.02	4.44	13

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TABLE 1(a) (continued)

	2 θ	d/n	Int.
5	20.15	4.41	12
	21.02	4.23	9
	21.48	4.14	11
	21.75	4.09	16
	22.28	3.99	14
10	22.60	3.93	33
	23.60	3.77	25
	24.60	3.62	6
	24.84	3.58	10
	25.10	3.55	11
15	25.88	3.44	67
	26.83	3.32	15
	27.64	3.23	20
	28.47	3.14	16
20	29.00	3.08	1
	29.54	3.02	3
	31.42	2.85	3
	32.15	2.78	4
	33.23	2.70	7
25	34.22	2.62	3

TABLE 1 (b)

	2 θ	d/n	Int.
30	7.08	12.49	40
	7.89	11.21	25
	8.89	9.95	6
	9.91	8.93	46
35	11.43	7.74	1
	12.80	6.92	9
	14.00	6.33	Sh
	14.22	6.23	35
40	14.68	6.03	13
	15.87	5.58	17
	17.75	5.00	2
	18.95	4.68	6
	19.38	4.58	10
45	19.58	4.53	9
	20.05	4.43	13
	20.15	4.41	Sh
	21.00	4.23	5
50	21.49	4.13	10
	21.78	4.08	17
	22.30	3.99	Sh
	22.58	3.94	35
	23.59	3.77	25
55	24.55	3.63	Sh
	24.82	3.59	10
	25.07	3.55	5

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TABLE 1 (b) (continued)

2 θ	d/n	Int.
25.85	3.45	68
26.48	3.37	3
26.85	3.32	16
27.64	3.23	19
28.46	3.14	14
28.98	3.08	3
29.60	3.02	4
31.42	2.85	4
32.18	2.78	5
33.21	2.70	7
34.22	2.62	2

[0025] As can be seen in Tables 1(a) and 1(b), X-ray diffraction patterns of the as synthesized SSZ-25 will vary.

[0026] After calcination, the SSZ-25 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table 2 below:

TABLE 2

2 θ	d/n	I/I ₀
3.4	25.5	17
7.19	12.30	100
8.04	11.00	55
10.06	8.78	63
14.35	6.17	40
16.06	5.51	17
22.77	3.90	38
23.80	3.74	20
26.08	3.417	65

[0027] The X-ray powder diffraction patterns were determined by standard techniques. The radiation was the K-alpha/doublet of copper and a scintillation counter spectrometer with a strip-chart pen recorder was used. The peak heights I and the positions, as a function of 2 θ where θ is the Bragg angle, were read from the spectrometer chart. From these measured values, the relative intensities, 100I/I₀, where I₀ is the intensity of the strongest line or peak, and d, the interplanar spacing in Angstroms corresponding to the recorded lines, can be calculated. Variations in the diffraction pattern can result from variations in the organic component used in the preparation and from variations in the silica-to-alumina mole ratio from sample to sample. The zeolite produced by exchanging the metal or other cations present in the zeolite with various other cations yields a similar diffraction pattern, although there can be shifts in interplanar spacing as well as variations in relative intensity. Calcination can also cause shifts in the X-ray diffraction pattern. Notwithstanding these perturbations, the basic crystal lattice structure remains unchanged.

[0028] Zeolites can be suitably prepared from an aqueous solution containing sources of an alkali metal oxide, an organic component mixture, an oxide of aluminum, gallium, iron, boron, titanium or mixtures thereof, and an oxide of silicon or germanium, or mixture of the two. The reaction mixture should have a composition in terms of mole ratios falling within the following ranges:

	Broad	Preferred
M/YO ₂	0.01-0.50	0.10-0.20
OH ⁻ /YO ₂	0.01-0.60	0.10-0.30
H ₂ O/YO ₂	10-120	20-50
Q/YO ₂	0.02-1.00	0.02-0.10
YO ₂ /W ₂ O ₃	10-200	15-120
Z/YO ₂	0.05-1.00	0.20-0.40

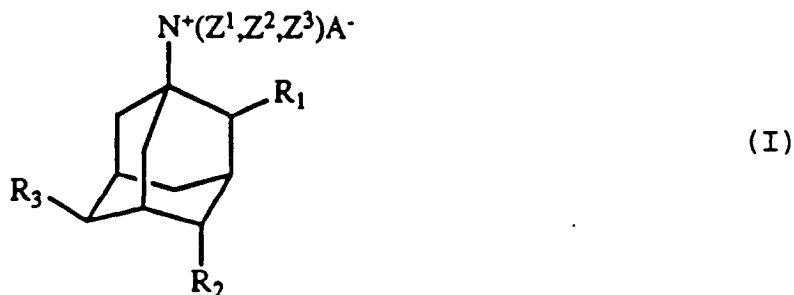
where M is an alkali metal, preferably sodium or potassium; Y is silicon, germanium, or both; Q is an adamantane-component comprising at least one compound chosen from the group consisting of adamantane quaternary ammonium ions and polar adamantyl derivatives, Z is an amine component comprising at least one amine chosen from amines containing from one to eight carbon atoms, ammonium hydroxide and mixtures thereof; and W is aluminum, gallium, iron, boron, titanium or mixtures thereof.

[0029] The reaction mixture can also be seeded with as-made zeolite crystals both to direct and accelerate the crystallization, as well as to minimize the formation of undesired aluminosilicate contaminants.

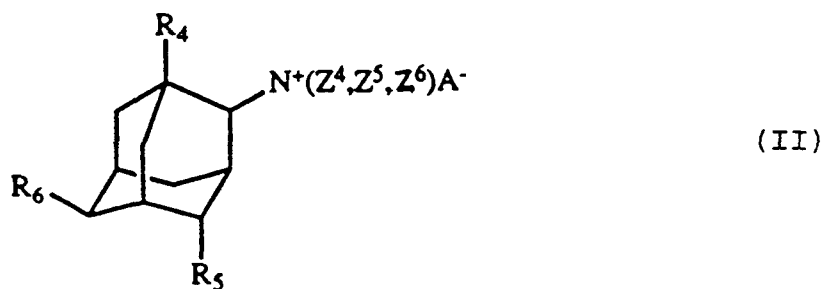
[0030] By "polar adamantyl derivative" is meant adamantyl compounds which contain either (a) a nitrogen atom that can bear a lone pair of electrons or an electropositive charge, or (b) an hydroxyl substituent. By "adamantane quaternary ammonium ions" is meant adamantane materials containing a nitrogen atom which is chemically bonded to four substituents, at least three of which are methyl groups and at least one of which is an adamantyl compound. By an "adamantane compound" or "adamantane component" is meant a composition comprising at least one compound chosen from the group consisting of adamantane quaternary ammonium ions and polar adamantyl derivatives. By "amine component" is meant at least one amine chosen from the group of amines having from one to eight carbon atoms, ammonium hydroxide or mixtures thereof. Preferably, the amine is an aliphatic or cycloaliphatic amine containing no more than 8 carbon atoms and mixtures thereof. By "organic component mixture" is meant a mixture comprising the organic templating compound and the amine component. By "seed material" is meant a material which reduces growth times of the zeolite crystals. One example of a seed material for SSZ-25 is as-made-SSZ-25. By "SSZ-25" is meant a material consisting substantially of the crystalline material with an X-ray diffraction pattern corresponding substantially to that of Table 2 after calcination of the as-made material.

[0031] The reaction mixture is prepared using standard zeolitic preparation techniques. Typical sources of aluminum oxide for the reaction mixture include aluminates, alumina, hydrated aluminum hydroxides, and aluminum compounds such as AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$. Typical sources of silicon oxide include silica hydrogel, silicic acid, colloidal silica, tetraalkyl orthosilicates, silica hydroxides, and fumed silicas. Gallium, iron, boron, titanium and germanium can be added in forms corresponding to their aluminum and silicon counterparts. Trivalent elements stabilized on silica colloids are also useful reagents.

[0032] The organic component mixture used to prepare SSZ-25 may contain adamantane quaternary ammonium ions. The adamantane quaternary ammonium ions are derived from a compound of the formula:



wherein each of Z^1 , Z^2 and Z^3 independently is lower alkyl and most preferably methyl; A^0 is an anion which is not detrimental to the formation of the zeolite; and each of R^1 , R^2 and R^3 independently is hydrogen, or lower alkyl and most preferably hydrogen; and



wherein each of R^4 , R^5 and R^6 independently is hydrogen or lower alkyl; and most preferably hydrogen; each of Z^4 , Z^5 and Z^6 independently is lower alkyl and most preferably methyl; and A^θ is an anion which is not detrimental to the formation of the zeolite. Mixtures of compounds having formula (I) and/or (II) can also be used. By "lower alkyl" is meant alkyl of from about 1 to 5 carbon atoms.

[0033] A^θ is an anion which is not detrimental to the formation of the zeolite. Representative of the anions include halide, e.g., fluoride, chloride, bromide and iodide, hydroxide, acetate, sulfate, carboxylate, etc. Hydroxide is the most preferred anion. It may be beneficial, for example, to ion-exchange the halide for hydroxide ion, thereby reducing the alkali metal hydroxide quantity required.

[0034] The adamantane quaternary ammonium compounds are prepared by methods known in the art.

[0035] The organic component mixture used to prepare SSZ-25 may contain a polar adamantyl derivative. The polar adamantyl derivative is commercially available and includes compounds such as 1-adamantanamine, 2-adamantanamine, 1-aminomethyl adamantane, 1-adamantanol, 2-adamantanol and mixtures of such compounds. Use of the polar adamantyl derivative instead of adamantane quaternary ammonium ions permits a reduction of production cost when making SSZ-25.

[0036] The organic component mixture used to prepare SSZ-25 also contains an amine component comprising at least one amine chosen from amines containing from one to eight carbon atoms, ammonium hydroxide and mixtures thereof. These amines are smaller than the organic templating compound used to prepare the zeolite. As used herein, the term "smaller", when used with respect to the amine component, means that the amine is lower in molecular weight than the organic templating compound and typically is no larger physically than the organic templating compound. Non-exclusive examples of these amines include isopropylamine, isobutyl amine, n-butylamine, piperidine, 4-methylpiperidine, cyclohexylamine, 1,1,3,3-tetramethyl butyl amine and cyclopentylamine and mixtures of such amines.

[0037] Use of these amines permits a reduction in the amount of the adamantane compound (or other organic templating compound) used, and significant cost savings result. In fact, it has quite surprisingly been found that, by using the amine component of the present invention, the amount of organic templating compound can be reduced to a level below that which is required to fill the micropore volume of the zeolite. In addition, use of these amines unexpectedly promotes faster growth times when used in combination with seed material.

[0038] In the previous SSZ-25 synthesis that relied completely on the quaternized adamantammonium derivative in larger quantity, a minimum of usually 160 hours was required to obtain the crystallized SSZ-25. By using an adamantane compound in conjunction with an amine component and seed material, crystallization periods of approximately 50 hours have been observed. A significant cost reduction in commercial use will occur as a result of the substantial reduction in crystallization period, since less equipment time is needed to grow SSZ-25 for a given production rate.

[0039] The reaction mixture used to prepare SSZ-25 can be seeded with material such as SSZ-25 crystals both to direct, and accelerate the crystallization, as well as to minimize the formation of undesired aluminosilicate contaminants.

[0040] The preferred reaction mixture for making SSZ-25 comprises 1-adamantanamine, isobutylamine, and SSZ-25 seeds as formulated in Example 17.

[0041] The reaction mixture is maintained at an elevated temperature until the crystals of the zeolite are formed. The temperatures during the hydrothermal crystallization step are typically maintained from about 140°C to about 200°C, preferably from about 160°C to about 180°C, and most preferably from about 170°C to about 180°C. The crystallization period is typically greater than 1 day and preferably from about 2 days to about 5 days.

[0042] The hydrothermal crystallization is conducted under pressure and usually in an autoclave so that the reaction mixture is subject to autogenous pressure. The reaction mixture can be stirred during crystallization. During the hydrothermal crystallization step, the zeolite crystals can be allowed to nucleate spontaneously from the reaction mixture.

[0043] Once the zeolite crystals have formed, the solid product is separated from the reaction mixture by standard mechanical separation techniques such as filtration. The crystals are water-washed and then dried, e.g., at 90°C to 120°C for from 8 to 24 hours, to obtain the as-synthesized zeolite crystals. The drying step can be performed at atmospheric or subatmospheric pressures.

[0044] The synthetic zeolites can be used as synthesized or can be thermally treated. By "thermal treatment" is meant heating to a temperature from about 200°C to about 820°C, either with or without the presence of steam. Usually, it is desirable to remove the alkali metal cation by ion exchange and replace it with hydrogen, ammonium, or any desired metal ion. Thermal treatment including steam helps to stabilize the crystalline lattice from attack by acids. The zeolite can be leached with chelating agents, e.g., EDTA or dilute acid solutions, to increase the silica:alumina mole ratio. The zeolite can be used in intimate combination with hydrogenating components, such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal, such as palladium or platinum, for those applications in which a hydrogenation-dehydrogenation function is desired. Typical replacing cations can include metal cations, e.g., rare earth, Group IIA and Group VIII metals, as well as their mixtures. Of the replacing metallic cations, cations of metals such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are particularly preferred.

[0045] The hydrogen, ammonium, and metal components can be exchanged into the zeolite. The zeolite can also

be impregnated with the metals, or the metals can be physically intimately admixed with the zeolite using standard methods known to the art. Also, the metals can be occluded in the crystal lattice by having the desired metals present as ions in the reaction mixture from which the zeolite is prepared.

[0046] Typical ion exchange techniques involve contacting the synthetic zeolite with a solution containing a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, chlorides and other halides, nitrates, acetates, and sulfates are particularly preferred. Representative ion exchange techniques are disclosed in a wide variety of patents including U.S. Patent Nos. 3,140,249, issued July 7, 1964 to Plank et al., 3,140,251, issued July 7, 1964 to Plank et al., and 3,140,253, issued July 7, 1964 to Plank et al. Ion exchange can take place either before or after the zeolite is calcined.

[0047] Following contact with the salt solution of the desired replacing cation, the zeolite is typically washed with water and dried at temperatures ranging from 65°C to about 315°C. After washing, the zeolite can be calcined in air or inert gas at temperatures ranging from about 200°C to 820°C for periods of time ranging from 1 to 48 hours, or more, to produce a catalytically active product especially useful in hydrocarbon conversion processes.

[0048] Regardless of cations present in the synthesized form of the zeolite, the spatial arrangement of the atoms which form the basic crystal lattice of the zeolite remains essentially unchanged. The exchange of cations has little, if any, effect on the zeolite lattice structures.

[0049] The zeolites can be formed into a wide variety of physical shapes. Generally speaking, the zeolite can be in the form of a powder, a granule, or a molded product, such as extrudate having particle size sufficient to pass through a 2-mesh (Tyler) screen and be retained on a 400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion with an organic binder, the aluminosilicate can be extruded before drying, or dried or partially dried and then extruded. The zeolite can be composited with other materials resistant to the temperatures and other conditions employed in organic conversion processes. By "matrix material" is meant other materials with which the zeolite is combined to make catalyst particles. Such matrix materials may include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and metal oxides. The latter may occur naturally or may be in the form of gelatinous precipitates, sols, or gels, including mixtures of silica and metal oxides. Use of an active material in conjunction with the synthetic zeolite, i.e., combined with it, tends to improve the conversion and selectivity of the catalyst in certain organic conversion processes. Inactive materials can suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically without using other means for controlling the rate of reaction. Catalysts produced with zeolites or other components incorporated therein may be subject to further ion exchange steps, metal inclusion, thermal treatment, and other processing steps as previously discussed for the zeolite alone.

[0050] Frequently, zeolite materials have been incorporated into naturally occurring clays, e.g., bentonite and kaolin. These materials, i.e., clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength, because in petroleum refining the catalyst is often subjected to rough handling. This tends to break the catalyst down into powders which cause problems in processing.

[0051] Naturally occurring clays which can be composited with the synthetic zeolites of this invention include the montmorillonite and kaolin families, which families include the sub-bentonites and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Fibrous clays such as sepiolite and attapulgite can also be used as supports. Such clays can be used in the raw state as originally mined or can be initially subjected to calcination, acid treatment or chemical modification.

[0052] In addition to the foregoing materials, the zeolites can be composited with porous matrix materials and mixtures of matrix materials such as silica, alumina, titania, magnesia, silica:alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, titania-zirconia as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel.

[0053] The zeolites can also be composited with other zeolites such as synthetic and natural faujasites (e.g., X and Y), erionites, and mordenites. They can also be composited with purely synthetic zeolites such as those of the ZSM series. The combination of zeolites can also be composited in a porous inorganic matrix.

[0054] Zeolites are useful in hydrocarbon conversion reactions. Examples of these uses are described in U.S. Patent No. 4,826,667, issued May 2, 1989 to Zones et al., which is incorporated herein by reference.

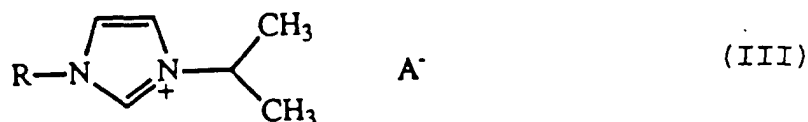
[0055] While the foregoing description has involved primarily the preparation of SSZ-25, it should be emphasized that other zeolites can be prepared using the method of this invention. For example, the zeolites known as SSZ-32, SSZ-28, EU-1, SSZ-35, ferrierite, ZSM-12 and ZSM-22 type structures have been successfully prepared in accordance with this invention. When it is desired to prepare these or other zeolites by the method of this invention, an organic templating compound capable of producing the desired zeolite in the presence of the amine component is employed.

[0056] In general, the mole ratios of the components of the reaction mixtures used to prepare these zeolites will be the same as, or very similar to, those described above with respect to SSZ-25, except, of course that the structure of the organic templating compound (Q) used will depend upon the zeolite desired to be made. Also, the composition of

the reaction mixture may vary slightly depending upon the zeolite desired to be made.

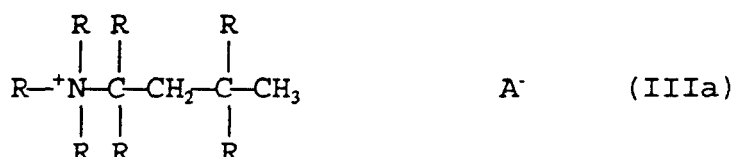
Zeolite SSZ-32

[0057] To prepare SSZ-32, an N-lower alkyl-N'-isopropylimidazolium cation may be used as the organic templating compound. These compounds have the general formula:



wherein R is lower alkyl containing 1 to 5 carbon atoms (preferably methyl or isopropyl) and A⁻ is an anion which is not detrimental to the formation of the zeolite. Representative anions include halogens, e.g., fluoride, chloride, bromide and iodide, hydroxide, acetate, sulfate, carboxylate, and the like. Hydroxide is the most preferred anion. The preferred N-lower alkyl-N'-isopropylimidazolium cations are N,N'-diisopropylimidazolium cation and N-methyl-N' isopropylimidazolium cation.

[0058] Another type of organic template which can be employed to prepare SSZ-32 are N,N,N-trialkyl-1,1,3,3-tetraalkylbutyl ammonium cations, which have the general formula:



where R and A are as defined above for formula III.

Preferably, R is methyl.

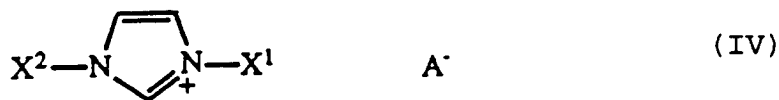
[0059] The as-made SSZ-32 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table A below:

TABLE A

2Theta	d/n	I/I ₀
8.04	10.99	30.2
8.81	10.03	12.6
11.30	7.82	23.1
18.08	4.90	8.0
19.56	4.53	61.2
20.81	4.26	65.1
22.75	3.90	100.0
23.89	3.72	85.6
24.59	3.62	34.9
25.16	3.53	21.9
25.91	3.43	41.8
26.89	3.31	7.2
28.13	3.17	11.5
29.30	3.04	5.9
31.48	2.84	6.0

ZSM-22 type zeolite

[0060] The organic templating compounds which may be used to prepare ZSM-22 type structures include imidazole salts characterized by the following formula:



wherein X^1 and X^2 independently represent a linear alkyl group containing from 1 to about 10 carbon atoms and $\text{A}^{\ominus}$ represents an anion which is not detrimental to the formation of the desired molecular sieve, such as those described above for formula (III).

[0061] The alkyl substitutions on the nitrogen atoms of the imidazole ring are any straight chain alkyl group having from 1 to about 10 carbon atoms. Thus, this moiety includes methyl, ethyl, propyl, n-butyl, as well as linear pentyl, hexyl, heptyl, octyl, nonyl, and decyl groups.

[0062] ZSM-22 type zeolites can also be prepared using piperidine derivatives as the organic templating compound. A preferred piperidine derivative is 2,6-dimethylpiperidine.

[0063] The as-made ZSM-22 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table B below:

TABLE B

2Theta	d/n	I/I ₀
8.13	10.87	37.7
10.15	8.70	4.0
12.72	6.95	18.6
16.51	5.36	2.6
19.36	4.58	3.0
20.28	4.38	100.0
24.11	3.69	75.3
24.53	3.63	75.2
25.64	3.47	63.9

Zeolite SSZ-28

[0064] To prepare SSZ-28, sources of an N,N-dimethyl-tropinium or N,N-dimethyl-3-azonium bicyclo[3.2.2]nonane cation may be used as the organic templating compound.

[0065] The as-made SSZ-28 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table C below:

TABLE C

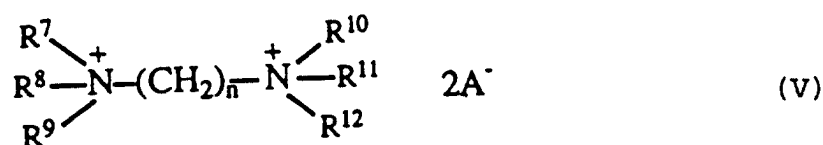
2Theta	d/n	I/I ₀
7.62	11.58	11.0
11.28	7.83	7.1
12.94	6.84	9.6
15.36	5.76	64.7
17.09	5.18	100.0
18.24	4.86	32.0
18.80	4.71	31.8
19.66	4.51	40.1
21.40	4.14	26.0

TABLE C (continued)

2Theta	d/n	I/I ₀
24.85	3.58	12.1
26.18	3.40	64.5
26.49	3.40	28.0
26.85	3.32	28.6
28.14	3.17	13.7
29.75	3.00	13.0

Zeolite EU-1

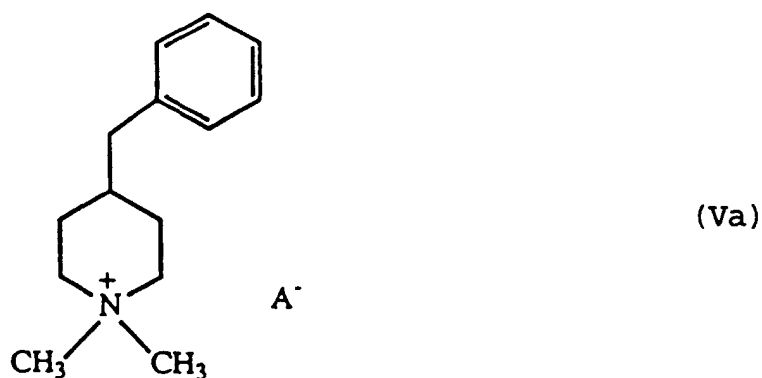
[0066] The organic templating compounds useful in preparing EU-1 are alkylated derivatives of a polymethylene α - ω diamine having the formula:



wherein n is in the range from 3 to 12 and R⁷ to R¹² which may be the same or different, can be alkyl or hydroxyalkyl groups, containing from 1 to 8 carbon atoms and up to five of the groups R⁷-R¹² can be hydrogen, and A⁻ represents an anion which is not detrimental to the formation of the desired zeolite, such as those described above for formula (III).

[0067] Preferred alkylated polymethylene diamine derivatives include alkylated hexamethylene diamines, especially methylated hexamethylene diamines, for example 1,6 N,N,N',N',N'-hexamethyl hexamethylene diammonium salts (e.g., halide, hydroxide, sulphate, silicate, aluminate).

[0068] Other organic templating compounds which can be used to prepare EU-1 in accordance with the present invention are 4-benzyl-N,N-dimethylpiperidinium compounds, which have the following structure:



where A⁻ represents an anion which is not detrimental to the formation of the desired molecular sieve, such as those described above for formula (III).

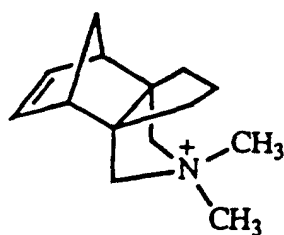
[0069] The as-made EU-1 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table D below:

TABLE D

2Theta	d/n	I/I ₀
7.92	11.15	48.3
8.70	10.15	21.5
9.06	9.75	6.0
12.87	6.87	2.3
19.04	4.65	39.7
20.53	4.32	100.0
22.15	4.01	61.8
23.26	3.82	31.8
23.94	3.71	20.0
25.97	3.43	9.3
26.52	3.36	9.4
27.29	3.26	34.8

Zeolite SSZ-35

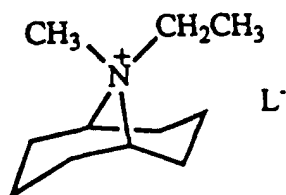
[0070] SSZ-35 can be prepared in accordance with the present invention using a polycyclic compound having the following formula as the organic templating compound:



(VI)

A⁻

where A⁻ is an anion which is not detrimental to the formation of the desired zeolite, such as those described above for formula (III). Another organic templating compound which may be used to prepare SSZ-35 in accordance with this invention is N-ethyl-N-methyl-9-azoniabicyclo[3.3.1]nonane which has the following structure:

L⁻

(VII)

where L⁻ is an anion which is not detrimental to the production of the molecular sieve, such as those described above for formula (III).

[0071] The anion for the salt may be essentially any anion such as halide or hydroxide which is not detrimental to the formation of the molecular sieve. As used herein, "halide" refers to the halogen anions particularly fluorine, chlorine, bromine, iodine, and combinations thereof. Thus, representative anions include hydroxide, acetate, sulfate, carboxylate, tetrafluoroborate, and halides, such as fluoride, chloride, bromide and iodide. Hydroxide and iodide are particularly preferred as anions.

[0072] The N-ethyl-N-methyl-9-azoniabicyclo[3.3.1]nonane templating compound used in making SSZ-35 is a conformationally constrained organic molecule. Altering the structure of this relatively rigid molecule can lead to a change in the molecular sieve obtained, presumably due to the differing steric demands of each template. However, increasing the steric requirements of the template may lead to a decrease in crystallization rate as well as a decrease in template

solubility in the reaction mixture. If the template is not sufficiently soluble, or if the template has particularly bulky substituent groups, it may be difficult to form crystals in the reaction mixture. Addition of a surfactant to the reaction mixture may help to solubilize the template.

[0073] The N-ethyl-N-methyl-9-azabicyclo[3.3.1]nonane templating compound may be synthesized by conventional techniques. In general, this template can be prepared in an efficient manner by condensing glutardialdehyde with a primary amine and acetone-dicarboxylic acid, all of which are readily available, inexpensive reagents. The intermediate formed is the 2,4-dicarboxy-3-keto-9-aza-bicyclononane, a di- β -ketoester which is easily decarboxylated upon treatment with acid. The 3-keto-moiety is removed by a classic Wolff-Kishner reduction (hydrazine, triethylene glycol, potassium hydroxide), and the desired quaternary ammonium salt is obtained by reaction of the resulting amine with an alkyl halide. Following purification by recrystallization, the halide salt can be ion-exchanged to the corresponding hydroxide salt using an ion-exchange resin.

[0074] The as-made SSZ-35 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table E below:

TABLE E

2Theta	d/n	I/I ₀
7.99	11.05	100.0
9.65	9.16	7.4
15.37	5.76	17.0
18.88	4.69	43.7
19.32	4.59	62.6
19.82	4.48	30.1
21.60	4.11	17.8
22.80	3.89	20.8
25.68	3.47	29.6
27.41	3.25	27.3
29.20	3.06	17.6

Zeolite ZSM-12

[0075] Zeolite ZSM-12 can be prepared in accordance with this invention using a heterocyclic compound having the following formula as the organic templating compound:



wherein L⁻ is an anion which is not detrimental to the formation of the ZSM-12.

[0076] The as-made ZSM-12 zeolite has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table F below:

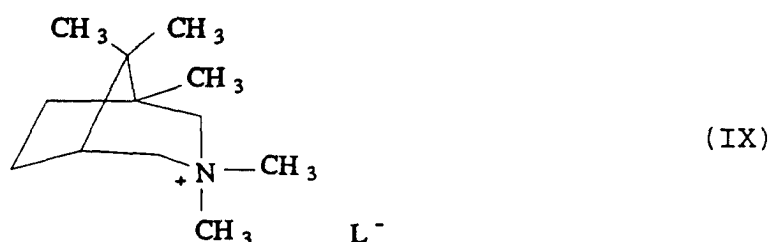
TABLE F

2Theta	d	I/I ₀ x 100
7.43	11.05	24.4
8.70	10.15	9.5
18.87	4.70	15.6

TABLE F (continued)

2Theta	d	I/I ₀ x 100
19.90	4.46	6.9
20.75	4.28	100.0
22.93	3.88	52.8
26.26	3.39	13.3
27.82	3.20	4.8
35.41	2.53	11.4

[0077] Another surprising aspect of this invention is that, when some organic templating compounds are used in combination with the amine component of this invention, a different zeolite structure is made than that which would be obtained in the absence of the amine component. For example, SSZ-35 has been made from organic templating compounds which are salts of 1,3,3,8,8-pentamethyl-3-azonia[3.2.1]octane. These compounds have a molecular structure of the general formula:



wherein L⁻ is an anion which is not detrimental to the formation of the zeolite. However, when these organic templating compounds are used in combination with the amine component of this invention, the resulting zeolite is SSZ-25.

[0078] Each organocation of this 1,3,3,8,8-pentamethyl-3-azonia[3.2.1]octane family has a charged quaternary ammonium heteroatom and two rings, one of which includes the quaternary ammonium heteroatom as a bridging unit. The anion for the salt may be essentially any anion such as halide or hydroxide which is not detrimental to the formation of the molecular sieve. As used herein, "halide" refers to the halogen anions particularly fluorine, chlorine, bromine, iodine, and combinations thereof. Thus, representative anions include hydroxide, acetate, sulfate, carboxylate, tetrafluoroborate, and halides such as fluoride, chloride, bromide, and iodide. Hydroxide and iodide are particularly preferred as anions.

[0079] Many of the organocation salts which have been disclosed in the prior art for use as templates for molecular sieve synthesis are conformationally flexible. These molecules can adopt many conformations in aqueous solution, and several templates can give rise to a single crystalline product. In contrast, the 1,3,3,8,8-pentamethyl-3-azoniabicyclo[3.2.1]octane templating compounds described above used to make SSZ-25 are conformationally constrained organic molecules.

[0080] These 1,3,3,8,8-pentamethyl-3-azoniabicyclo[3.2.1]octane compounds can be prepared by converting camphoric anhydride to the corresponding N-methyl imide using methyl amine. The imide can be reduced to N-methylcamphidine upon reduction with lithium aluminum hydride in ether, and the desired quaternary ammonium salt obtained by treatment with methyl iodide. Following purification by recrystallization, the halide salt can be ion-exchanged to the corresponding hydroxide salt using an ion-exchange resin.

EXAMPLES

Example 1

Preparation of N,N,N-Trimethyl-1-adamantanammonium Hydroxide (Template A)

[0081] Ten (10) grams of 1-adamantanamine (Aldrich) was dissolved in a mixture of 29 gms tributylamine and 60 mls dimethylformamide. The mixture was chilled in an ice bath.

[0082] 28.4 Grams of methyl iodide were added dropwise to the chilled solution with continuous stirring. After several hours, crystals appear. The reaction was continued overnight and allowed to come to room temperature. The crystals were filtered and washed with tetrahydrofuran and then diethyl ether before vacuum drying. Additional product was

obtained by adding enough diethyl ether to the reaction filtrate to produce two phases and then with vigorous stirring acetone was added until the solution just became one phase. Continued stirring produced crystallization at which time the solution can be chilled to induce further crystallization. The product has a melting point near 300°C (decomp.) and the elemental analyses and NMR are consistent with the known structure. The vacuum-dried iodide salt was then ion-exchanged with ion-exchange resin AG 1X8 (in molar excess) to the hydroxide form. The exchange was performed over a column or more preferably by overnight stirring of the resin beads and the iodide salt in an aqueous solution designed to give about a 0.5 molar solution of the organic hydroxide. This produces Template A.

Example 2

Preparation of N,N,N-Trimethyl-2-adamantanammonium Hydroxide (Template B)

[0083] Five (5) grams of 2-adamantanone (Aldrich Chemical Co.) was mixed with 2.63 gms of formic acid (88%) and 4.5 gms of dimethyl formamide. The mixture was then heated in a pressure vessel for 16 hours at 190°C. Care should be taken to anticipate the increase in pressure the reaction experiences due to CO₂ evolution. The reaction was conveniently carried out in a Parr 4748 reactor with teflon liner. The workup consists of extracting N,N-dimethyl-2-adamantanamine from a basic (pH=12) aqueous solution with diethyl ether. The various extracts were dried with Na₂SO₄, the solvent removed and the product taken up in ethyl acetate. An excess of methyl iodide was added to a cooled solution which was then stirred at room temperature for several days. The crystals were collected and washed with diethyl ether to give N,N,N-trimethyl-2-adamantanammonium iodide. The product is checked by microanalysis for C, H, and N. The conversion to the hydroxide form was carried out analogously to Template A above.

Example 3

Synthesis of SSZ-25

[0084] 0.50 Grams of a 0.55 molar solution of Template B and 0.22 gms of isobutyl amine and 0.03 gms of SSZ-25 seeds were mixed with 0.20 gms KOH(s), 0.083 gms of Reheis F-2000 hydrated alumina (50-56 wt% aluminum oxide), and 11.4 MI H₂O. After thorough mixing, 0.90 gms of Cabosil M5 was blended in as silica source. The reaction mixture was heated in the Teflon cup of a Parr 4745 reactor at 170°C at 43 rpm for 4 days. Workup produced crystalline SSZ-25.

Example 4

Synthesis of SSZ-25

[0085] In this example, the use of a nonquaternized amine is demonstrated. The same experiment was run as in Example 3, except 1 millimole of 1-adamantanamine (Aldrich) replaced the Template B. The product was again SSZ-25.

Example 5

Synthesis of SSZ-25

[0086] This example also demonstrates the use of a nonquaternized amine. 12.5 Grams of Reheis F-2000 was dissolved in 30 gms of KOH(s) and 1500 M1 H₂O, 7.5 gms of 1-adamantanamine (Aldrich Chemical Co.), and 75 gms of 4-methylpiperidine (Aldrich Chemical Co.). 3 Grams of SSZ-25 seed crystals and 437 gms of Ludox AS-30 were added last. The reaction was run in a 1-gallon autoclave with Hastelloy C liner at 170°C and 75 rpm. After 6 days, the product was crystalline SSZ-25.

[0087] Refer to Table 3 for a summary of Examples 3-5.

TABLE 3

Ex. No.	Adamantyl Component	Amine	Product
3	Template B	Isobutyl Amine	SSZ-25
4	1-adamantanamine	Isobutyl Amine	SSZ-25
5	1-adamantanamine	4-methylpiperidine	SSZ-25

Examples 6-9

Synthesis of SSZ-25

[0088] In these examples, the effectiveness or necessity of the adamantyl quaternary ammonium ion is demonstrated by comparison of reaction products with and without such a component at only a 0.02 molar ratio to silica. This quantity of adamantyl component is insufficient to fill the micropore volume of the growing SSZ-25 and additional organic is needed, and was subsequently found in the micropore system. Table 4 shows the comparative examples.

TABLE 4

SSZ-25 Syntheses With and Without Adamantyl Quaternary Ammonium Ion Synthesis Promoters ^(a)					
Ex. No.	Adamantyl Component	Amine ^(b)	SiO ₂ / Al ₂ O ₃	KOH/SiO ₂	Product
6	B	Piperidine	35	0.20	SSZ-25
7	-	Piperidine	35	0.20	ZSM-5
8	B	Cyclopentylamine	35	0.20	SSZ-25
9	-	Cyclopentylamine	35	0.20	ZSM-5

^(a) Experiments carried out as in Example 3.

^(b) Experiments carried out using amine/SiO₂ ratio of 0.20. B = Template B (Example 2).

Examples 10-12

Synthesis of SSZ-25

[0089] In these experiments, the variation of the adamantane compound is demonstrated. The experiments are carried out as in Example 3. Recall that in Example 7, the use of piperidine alone, even in the presence of SSZ-25 seeds, produced ZSM-5.

[0090] Refer to Table 5 for the variations of the adamantane compound.

TABLE 5

Ex. No.	Adamantyl Component*	Piperidine/SiO ₂	SiO ₂ / Al ₂ O ₃	KOH/SiO ₂	Product
10	A	0.20	35	0.20	SSZ-25
11	C	0.20	35	0.20	SSZ-25
12	D	0.20	35	0.20	SSZ-25

*At a level of 0.02 relative to SiO₂.

A = Template A (Example 1).

C = Quaternized derivative of 1-aminomethyl-adamantane.

D = 1-adamantanol.

Examples 13-20

Synthesis of SSZ-25

[0091] In these examples, SSZ-25 was formulated, using SSZ-25 as a seed material in two examples and using no seed in two examples to determine whether seed material was necessary to produce SSZ-25. The final product was SSZ-25 in all cases. In the examples where 4-methylpiperidine was used as the amine component, improvement in growth time was observed at three days for the example utilizing seed material. In the examples where isobutylamine was used as the amine component, the growth time was improved by at least a factor of two for the example utilizing seed material.

[0092] In these examples, 1 millimole of 1-adamantanamine was mixed with 15 millimoles of silica as SiO₂ and 3 millimoles of the smaller amine. All of the remaining ratios of reactants and run conditions were as in Example 3. In Examples 13-16, the major amine was 4-methylpiperidine. For Examples 17-20, the major amine was isobutylamine. Reaction conditions were substantially the same as those in Example 3. Results are summarized in Table 6.

TABLE 6

Effect of seed on type of zeolite produced and growth time for SSZ-25				
Ex. No.	Amine Component	Seed Used	Growth Time	Product
13	4-methylpiperidine	SSZ-25	3 days	SSZ-25 + amorphous
14	4-methylpiperidine	SSZ-25	6 days	SSZ-25
15	4-methylpiperidine	none	3 days	amorphous
16	4-methylpiperidine	none	6 days	SSZ-25
17	isobutylamine	SSZ-25	3 days	SSZ-25
18	isobutylamine	SSZ-25	6 days	SSZ-25
19	isobutylamine	none	3 days	SSZ-25 + amorphous
20	isobutylamine	none	6 days	SSZ-25

Examples 21-28Synthesis of SSZ-32

[0093] A basic reaction solution was made by combining 0.50 millimoles of N,N'-diisopropylimidazolium hydroxide (Template E), 0.20 gram of solid KOH, 0.083 gram of Reheis F-2000 hydrated aluminum hydroxide, and a total of 11.4 ml of water. To this solution, 0.90 gram of Cabosil M-5 fumed silica (98%) was added. Finally, 0.20 gram of isobutyl amine was added. These reactants were all combined in the Teflon cup of a Parr 4745 reactor (23 ml capacity). The reactor was sealed and loaded onto a rotating spit in a Blue M oven and heated at 170°C for 6 days while rotating at 43 rpm. After this time period, the reactor was cooled in air, the resulting solid product filtered and washed with water in a funnel, and then air-dried. The resulting powder was analyzed by X-ray diffraction (XRD) and found to be SSZ-32. An elemental analysis showed the SiO₂/Al₂O₃ ratio for this product to be 28.

[0094] This reaction was repeated using each in turn the amines listed in Table 7 below in the quantities also shown in that table. The product of each reaction was SSZ-32.

TABLE 7

Example No.	Amine	Amount of Amine
22	methylamine	0.5g*
23	NH ₄ OH	0.66g**
24	butylamine	0.20g
25	t-butylamine	0.25g
26	dipropylamine	0.22g
27	isopropylamine	0.20g
28	cyclopentylamine	0.26g

*40% aqueous solution

**30% aqueous solution

[0095] These examples demonstrate that SSZ-32 can be prepared using very low levels of the organic templating compound, in this case a mole ratio of Template E/SiO₂ of only 0.033. In fact, this reaction has been successfully conducted with this ratio as low as 0.02. Without the addition of the small amine (isobutyl amine) the product, SSZ-32, would not be achieved at this low level of templating compound.

Example 29-39

[0096] A procedure similar to that described in Examples 21-28 was used to prepare the zeolites listed in the table below except that the organic template was N,N,N-trimethyl-1,1,3,3-tetramethyl butyl ammonium hydroxide (Template E') and the amines were those listed in the table below.

[0097] The reaction mixture contained the following mole ratios:

Template E'/SiO₂ = 0.02

Amine/SiO₂ = 0.20

[0098] Also, the reaction mixture contained 0.6 wt. % SSZ-32 seed crystals.

Ex No.	Amine	Growth Time	Product
29*	isobutylamine	9 days	SSZ-32 (plus trace amorphous)
30*	cyclopentylamine	9 days	SSZ-32
31*	isopropylamine	7 days	SSZ-32
32*	n-butylamine	7 days	ZSM-5 (plus minor amount of ferrierite)
33*	piperidine	7 days	ZSM-5
34*	cyclohexylamine	18 days	ferrierite (plus minor amount of cristobalite)
35*	1,1,3,3-tetramethylbutyl amine	7 days	SSZ-32
36**	isobutylamine	6 days	SSZ-32 (plus trace cristobalite)
37**	isopropylamine	7 days	SSZ-32 (plus cristobalite)
38**	n-butylamine	7 days	cristobalite + ZSM-5 + quartz
39**	piperidine	7 days	ZSM-5 (plus amorphous material)

* Silica source was Nyacol colloidal silica.

** Silica source was Cabosil fumed silica.

Example 40

Synthesis of SSZ-28

[0099] The same reaction as described in Example 21 for SSZ-32 was carried out, but with the following changes. The organic templating compound was N,N-dimethyl-3-azonium bicyclo [3.2.2] nonane hydroxide (Template F), and the ratio of Template F/SiO₂ was 0.05 (i.e., 0.75 millimoles of Template F was used in the reaction). The resulting product was found to be SSZ-28 by XRD.

[0100] This example also demonstrates that zeolites can be prepared by the method of this invention using very low amounts of organic templating compound.

Example 41

Synthesis of EU-1

[0101] The same reaction using the same molar quantities described in Example 40 was carried out with the exception that the organic templating compound was the diquatery ammonium compound 1,6-N,N,N,N',N'-hexamethyl hexamethylene diammonium hydroxide (Template G). The resulting product was analyzed by XRD and found to be zeolite EU-1.

Example 42

Synthesis of EU-1

[0102] 0.62 Gram of a solution of 4-benzyl-N,N-dimethylpiperidinium hydroxide (0.485 mmol OH/g), 0.08 gram of Reheis F2000 hydrated aluminum hydroxide, and 0.20 gram of solid KOH were dissolved in 11.4 grams of water. Isobutyl amine (0.22 gram) was added to this solution, followed by the addition of 0.90 gram of Cabosil M-5 fumed silica. The resulting reaction mixture was mixed thoroughly and sealed in a Parr 4745 reactor which was then heated to 170°C and rotated at 43 rpm. After 16 days the reaction was complete, and the product which was isolated was determined by XRD to be EU-1.

Example 43

Synthesis of SSZ-35

[0103] The same reaction using the same molar quantities described in Example 40 was carried out, except that the organic templating compound used was the polycyclic compound having formula VI above (Template H). The resulting product was determined by XRD to be SSZ-35.

Example 44Synthesis of ZSM-22 type structures

[0104] The same reaction described in Example 21 was carried out, except that the organic templating compound was 2,6-dimethylpiperidine (Template I) which was used in the ratio of Template I/SiO₂ of 0.02. The resulting product was determined by XRD to be ZSM-22 type structures.

Example 45

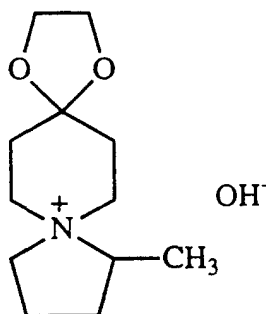
[0105] Using the procedure of Example 21 and the amines and organic templating compounds shown in Table 8, the zeolites also shown in Table 8 were prepared.

TABLE 8

Zeolite	Amine	Amount of Amine	Template
SSZ-28	cyclopentylamine	0.26g	F
SSZ-25	piperidine	0.26g	F
EU-1	cyclopentylamine	0.26g	G
SSZ-35	cyclopentylamine	0.26g	H
SSZ-35	piperidine	0.26g	H
ZSM-22	cyclopentylamine	0.26g	I
ZSM-22	piperidine	0.26g	I

Example 46Synthesis of ZSM-12

[0106] The same procedure described in Example 21 was performed, except that a piperidine-based templating agent (Template J) having the following structure:



was used in place of the imidazolium-based template employed in Example 21. After 23 days of heating at 170°C, the product was isolated and identified as ZSM-12. Elemental analysis showed the product to have a SiO₂/Al₂O₃ mole ratio of 30.

Claims

1. A method for preparing a zeolite selected from the group consisting of large pore zeolites, medium pore zeolites having unidimensional channels, and small pore zeolites, said method comprising:

A. forming an aqueous reaction mixture comprising (1) a source of an oxide selected from silicon oxide, ger-

manium oxide and mixtures thereof; (2) a source of an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide and mixtures thereof; (3) a source of an alkali metal oxide; (4) an amine component comprising at least one amine chosen from the group of: amines containing one to eight carbon atoms; ammonium hydroxide; and mixtures thereof, and (5) an organic templating compound capable of forming said zeolite in the presence of said amine, wherein said amine is smaller than said organic templating compound and wherein said organic templating agent is used in an amount less than that required to crystallize the zeolite in the absence of said amine component ; and

B. maintaining said aqueous mixture under sufficient crystallization conditions until crystals are formed.

2. The method of Claim 1 wherein the large pore zeolite has unidimensional channels.
3. The method of Claim 1 wherein the large pore zeolite has multidimensional channels.
4. The method of Claim 1 wherein said organic templating compound is selected from the group consisting of quaternary ammonium ions, cyclic amines and polar adamantyl derivatives.
5. The method of Claim 1 wherein the amine component comprises an aliphatic, cycloaliphatic or heterocyclic amine, ammonium hydroxide or mixtures thereof.
6. The method of Claim 5 wherein the amine component comprises a compound selected from the group consisting of isobutylamine, methylamine, ammonium hydroxide, butylamine, t-butylamine, dipropylamine, isopropylamine, cyclopentylamine, piperidine, 4-methylpiperidine, cyclohexylamine, and 1,1,3,3-tetramethylbutyl amine.
7. The method of Claim 1 wherein said aqueous mixture further comprises seeds of zeolite crystals in an amount sufficient to direct and accelerate crystallization.
8. The method of Claim 1 wherein the reaction mixture comprises the following in terms of mole ratios:

M/YO ₂	0.01-0.50
OH/YO ₂	0.01-0.60
H ₂ O/YO ₂	10-120
Q/YO ₂	0.02-1.00
YO ₂ /W ₂ O ₃	10-200
Z/YO ₂	0.05-1.00

where M is an alkali metal, Y is silicon, germanium, or both; Q is the organic templating compound, Z is the amine component; and W is aluminum, gallium, iron, boron, titanium or mixtures thereof.

9. The method of claim 8 wherein the reaction mixture comprises the following in terms of mole ratios:

M/YO ₂	0.10-0.20
OH/YO ₂	0.10-0.30
H ₂ O/YO ₂	20-50
Q/YO ₂	0.02-0.10
YO ₂ /W ₂ O ₃	15-120
Z/YO ₂	0.20-0.40

10. The method of claim 4 wherein the zeolite has, after calcination, the X-ray diffraction pattern of the following Table 2:

TABLE 2

2 θ	d/n	I/I ₀
3.4	25.5	17
7.19	12.30	100
8.04	11.00	55

TABLE 2 (continued)

2 θ	d/n	I/I _o
10.06	8.78	63
14.35	6.17	40
16.06	5.51	17
22.77	3.90	38
23.80	3.74	20
26.08	3.417	65

11. The method of claim 10 wherein the organic templating compound comprises adamantanamine.
12. The method of claim 11 wherein said adamantanamine comprises at least one adamantanamine from the group 1-adamantanamine or 2-adamantanamine.
13. The method of claim 11 wherein the amine component comprises isobutylamine, 4-methylpiperidine, cyclopentylamine, or piperidine.
14. The method of claim 11 wherein the organic templating compound comprises adamantanol.
15. The method of claim 14 wherein said adamantanol comprises at least one adamantanol from the group 1-adamantanol and 2-adamantanol.
16. The method of claim 14 wherein the amine component comprises piperidine or isobutylamine.
17. The method of claim 4 wherein the as-synthesized zeolite has the X-ray diffraction pattern of the following Table A:

TABLE A

2Theta	d/n	I/I _o
8.04	10.99	30.2
8.81	10.03	12.6
11.30	7.82	23.1
18.08	4.90	8.0
19.56	4.53	61.2
20.81	4.26	65.1
22.75	3.90	100.0
23.89	3.72	85.6
24.59	3.62	34.9
25.16	3.53	21.9
25.91	3.43	41.8
26.89	3.31	7.2
28.13	3.17	11.5
29.30	3.04	5.9
31.48	2.84	6.0

18. The method of claim 17 wherein the organic templating compound comprises an N,N'-disubstituted imidazolium compound or N,N,N-trialkyl-1,1,3,3-tetraalkyl butyl ammonium cation.
19. The method of claim 18 wherein the imidazolium compound is an N,N'-diisopropylimidazolium cation, or N-methyl-N'-isopropylimidazolium cation.
20. The method of claim 18 wherein the N,N,N-trialkyl-1,1,3,3-tetraalkyl butyl ammonium cation is a N,N,N-trimethyl-1,1,3,3-tetramethylbutyl ammonium cation.
21. The method of claim 18 wherein the organic templating compound comprises an N,N'-disubstituted imidazolium

compound and the amine component comprises a compound selected from the group consisting of isobutylamine, methylamine, ammonium hydroxide, butylamine, t-butylamine, dipropylamine, isopropylamine, and cyclopentylamine.

22. The method of claim 18 wherein the organic templating compound comprises an N,N,N-trialkyl-1,1,3,3-tetraalkyl butyl ammonium cation and the amine component is selected from the group consisting of isobutylamine, cyclopentylamine, isopropylamine and 1,1,3,3-tetramethylbutyl amine.

23. The method of claim 4 wherein the zeolite has, in the as-synthesized form, the X-ray diffraction pattern of the following Table B:

TABLE B

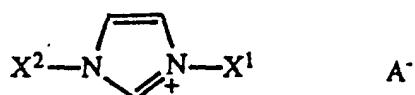
2Theta	d/n	I/I ₀
8.13	10.87	37.7
10.15	8.70	4.0
12.72	6.95	18.6
16.51	5.36	2.6
19.36	4.58	3.0
20.28	4.38	100.0
24.11	3.69	75.3
24.53	3.63	75.2
25.64	3.47	63.9

24. The method of claim 23 wherein the organic templating compound comprises a piperidine derivative.

25. The method of claim 24 wherein the piperidine derivative is 2,6-dimethylpiperidine.

26. The method of claim 24 wherein the amine component comprises isobutylamine, cyclopentylamine or piperidine.

27. The method of claim 23 wherein the organic templating compound comprises imidazole salts of the formula



wherein X¹ and X² independently represent a linear alkyl group containing from 1 to about 10 carbon atoms, and A^θ represents an anion which is not detrimental to the formation of the zeolite.

28. The method of claim 4 wherein the zeolite has, in the as-synthesized form, the X-ray diffraction pattern of the following Table C:

TABLE C

2Theta	d/n	I/I ₀
7.62	11.58	11.0
11.28	7.83	7.1
12.94	6.84	9.6
15.36	5.76	64.7
17.09	5.18	100.0
18.24	4.86	32.0
18.80	4.71	31.8
19.66	4.51	40.1

TABLE C (continued)

2Theta	d/n	I/I ₀
21.40	4.14	26.0
24.85	3.58	12.1
26.18	3.40	64.5
26.49	3.40	28.0
26.85	3.32	28.6
28.14	3.17	13.7
29.75	3.00	13.0

29. The method of claim 28 wherein the organic templating compound is selected from the group consisting of N,N-dimethyltropinium and N,N-dimethyl-3-azonium bicyclo [3.2.2] nonane cations.

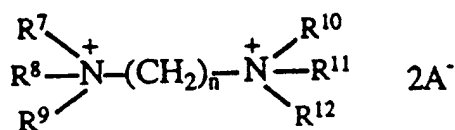
30. The method of claim 29 wherein the amine component comprises isobutylamine, cyclopentylamine, or piperidine.

31. The method of claim 4 wherein the zeolite has, in the as-synthesized form, the X-ray diffraction pattern of the following Table D:

TABLE D

2Theta	d/n	I/I ₀
7.92	11.15	48.3
8.70	10.15	21.5
9.06	9.75	6.0
12.87	6.87	2.3
19.04	4.65	39.7
20.53	4.32	100.0
22.15	4.01	61.8
23.26	3.82	31.8
23.94	3.71	20.0
25.97	3.43	9.3
26.52	3.36	9.4
27.29	3.26	34.8

32. The method of claim 31 wherein the organic templating compound comprises alkylated derivatives of a polymethylene diamine having the formula:



wherein n is in the range from 3 to 12, R⁷ to R¹², which may be the same or different, are hydrogen, alkyl or hydroxyalkyl groups, containing from 1 to 8 carbon atoms and up to five of the groups R⁷-R¹² can be hydrogen, and A⁻ is an anion which is not detrimental to the formation of the zeolite.

33. The method of claim 32 wherein the organic templating compound comprises a 1,6-N,N,N',N',N'-hexamethyl hexamethylene diammonium cation.

34. The method of claim 32 wherein the amine component comprises isobutylamine or cyclopentylamine.

35. The method of claim 31 wherein the organic templating compound is a 4-benzyl-N,N-dimethylpiperidinium com-

pound.

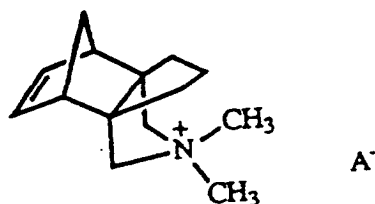
36. The method of claim 35 wherein the amine component comprises isobutylamine.

37. The method of claim 4 wherein the zeolite has, in the as-synthesized form, the X-ray diffraction pattern of the following Table E:

TABLE E

2Theta	d/n	I/I _o
7.99	11.05	100.0
9.65	9.16	7.4
15.37	5.76	17.0
18.88	4.69	43.7
19.32	4.59	62.6
19.82	4.48	30.1
21.60	4.11	17.8
22.80	3.89	20.8
25.68	3.47	29.6
27.41	3.25	27.3
29.20	3.06	17.6

38. The method of claim 37 wherein the organic templating compound is selected from the group consisting of an N-ethyl-N-methyl-9-azoniabicyclo [3.3.1] nonane cation and a compound having the following formula:



wherein A⁻ is an anion which is not detrimental to the formation of the zeolite.

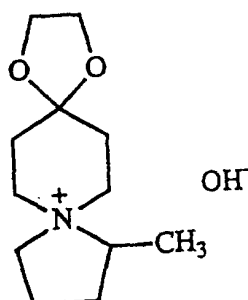
39. The method of claim 38 wherein the amine component comprises isobutylamine, cyclopentylamine or piperidine.

40. The method of claim 4 wherein the as-synthesized zeolite has the X-ray diffraction pattern of the following Table F:

TABLE F

2Theta	d	I/I _o × 100
7.43	11.05	24.4
8.70	10.15	9.5
18.87	4.70	15.6
19.90	4.46	6.9
20.75	4.28	100.0
22.93	3.88	52.8
26.26	3.39	13.3
27.82	3.20	4.8
35.41	2.53	11.4

41. The method of claim 40 wherein the organic templating compound comprises a compound having the following formula:



42. The method of claim 41 wherein the amine component comprises isobutylamine.

43. A zeolite selected from the group consisting of large pore zeolites, medium pore zeolites having unidimensional channels, and small pore zeolites having an as-synthesized molar composition in an anhydrous state of $(0.02 \text{ to } 2.0) \text{ Q} : (0.02 \text{ to } 1.0) \text{ Z} : (0.1 \text{ to } 2.0) \text{ M}_2\text{O} : \text{W}_2\text{O}_3 : (10 \text{ to } 200) \text{ YO}_2$, wherein M is an alkali metal cation; W is selected from aluminum, gallium, iron, boron, titanium and mixtures thereof; Y is selected from silicon, germanium, and mixtures thereof; Z is an amine component comprising at least one amine chosen from the group of: amines containing from one to eight carbon atoms; ammonium hydroxide; and mixtures thereof, Q is an organic templating compound capable of forming the zeolite in the presence of said amine component, wherein said amine is smaller than the organic templating compound, and wherein said organic templating agent is used in an amount less than that required to crystallize the zeolite in the absence of said amine component.

44. The zeolite of claim 43 having, after calcination, the X-ray diffraction pattern of the following Table 2:

TABLE 2

2 θ	d/n	I/I ₀
3.4	25.5	17
7.19	12.30	100
8.04	11.00	55
10.06	8.78	63
14.35	6.17	40
16.06	5.51	17
22.77	3.90	38
23.80	3.74	20
26.08	3.417	65

45. The zeolite of claim 43 having, in the as-synthesized form, the X-ray diffraction pattern of the following Table A:

TABLE A

2Theta	d/n	I/I ₀
8.04	10.99	30.2
8.81	10.03	12.6
11.30	7.82	23.1
18.08	4.90	8.0
19.56	4.53	61.2
20.81	4.26	65.1
22.75	3.90	100.0
23.89	3.72	85.6
24.59	3.62	34.9
25.16	3.53	21.9
25.91	3.43	41.8

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TABLE A (continued)

2Theta	d/n	I/I _o
26.89	3.31	7.2
28.13	3.17	11.5
29.30	3.04	5.9
31.48	2.84	6.0

46. The zeolite of claim 43 having, in the as-synthesized form, the X-ray diffraction pattern of the following Table B:

TABLE B

2Theta	d/n	I/I _o
8.13	10.87	37.7
10.15	8.70	4.0
12.72	6.95	18.6
16.51	5.36	2.6
19.36	4.58	3.0
20.28	4.38	100.0
24.11	3.69	75.3
24.53	3.63	75.2
25.64	3.47	63.9

47. The zeolite of claim 43 having, in the as-synthesized form, the X-ray diffraction pattern of the following Table C:

TABLE C

2Theta	d/n	I/I _o
7.62	11.58	11.0
11.28	7.83	7.1
12.94	6.84	9.6
15.36	5.76	64.7
17.09	5.18	100.0
18.24	4.86	32.0
18.80	4.71	31.8
19.66	4.51	40.1
21.40	4.14	26.0
24.85	3.58	12.1
26.18	3.40	64.5
26.49	3.40	28.0
26.85	3.32	28.6
28.14	3.17	13.7
29.75	3.00	13.0

48. The zeolite of claim 43 having, in the as-synthesized form, the X-ray diffraction pattern of the following Table D:

TABLE D

2Theta	d/n	I/I _o
7.92	11.15	48.3
8.70	10.15	21.5
9.06	9.75	6.0
12.87	6.87	2.3
19.04	4.65	39.7
20.53	4.32	100.0

TABLE D (continued)

2Theta	d/n	I/I _o
22.15	4.01	61.8
23.26	3.82	31.8
23.94	3.71	20.0
25.97	3.43	9.3
26.52	3.36	9.4
27.29	3.26	34.8

49. The zeolite of Claim 43 having, in the as-synthesized form, the X-ray diffraction pattern of the following Table E:

TABLE E

2Theta	d/n	I/I _o
7.99	11.05	100.0
9.65	9.16	7.4
15.37	5.76	17.0
18.88	4.69	43.7
19.32	4.59	62.6
19.82	4.48	30.1
21.60	4.11	17.8
22.80	3.89	20.8
25.68	3.47	29.6
27.41	3.25	27.3
29.20	3.06	17.6

50. The zeolite of claim 43 having, in the as-synthesized form, the X-ray diffraction pattern of the following Table F:

TABLE F

2Theta	d	I/I _o × 100
7.43	11.05	24.4
8.70	10.15	9.5
18.87	4.70	15.6
19.90	4.46	6.9
20.75	4.28	100.0
22.93	3.88	52.8
26.26	3.39	13.3
27.82	3.20	4.8
35.41	2.53	11.4

Patentansprüche

1. Verfahren zur Herstellung eines Zeoliths aus der Gruppe großporige Zeolithe, mittelporige Zeolithe mit eindimensionalen Kanälen und kleinporige Zeolithen, umfassend:

A. Herstellen eines wässrigen Reaktionsgemisches, umfassend:

- (1) eine Quelle für ein Oxid, ausgewählt aus Siliciumoxid, Germaniumoxid und Gemischen davon;
- (2) eine Quelle für ein Oxid, ausgewählt aus Aluminiumoxid, Galliumoxid, Eisenoxid, Boroxid, Titanoxid und Gemischen davon;
- (3) eine Quelle für ein Alkalimetalloxid;
- (4) eine Aminkomponente, die mindestens ein Amin umfasst, ausgewählt aus der Gruppe Amine mit 1

bis 8 Kohlenstoffatomen, Ammoniumhydroxid und Gemischen davon, und
(5) eine organische Templatverbindung, die den Zeolith in Gegenwart des Amins bilden kann, wobei das Amin kleiner ist als die organische Templatverbindung und die organische Templatverbindung in einer Menge verwendet wird, die kleiner ist als man zur Kristallisation des Zeoliths in Abwesenheit der Aminkomponente benötigt; und

B. Halten des wässrigen Gemisches unter hinreichenden Kristallisationsbedingungen, bis man Kristalle erhält.

2. Verfahren nach Anspruch 1, wobei der großporige Zeolith eindimensionale Kanäle hat.
3. Verfahren nach Anspruch 1, wobei der großporige Zeolith mehrdimensionale Kanäle hat.
4. Verfahren nach Anspruch 1, wobei die organische Templatverbindung ausgewählt ist aus der Gruppe, bestehend aus quartären Ammoniumionen, zyklischen Aminen und polaren Adamantyl-Derivaten.
5. Verfahren nach Anspruch 1, wobei die Aminkomponente umfasst ein aliphatisches, cycloaliphatisches oder heterozyklisches Amin, Ammoniumhydroxid oder Gemische davon.
6. Verfahren nach Anspruch 5, wobei die Aminkomponente eine Verbindung umfasst aus der Gruppe Isobutylamin, Methylamin, Ammoniumhydroxid, Butylamin, tert.-Butylamin, Dipropylamin, Isopropylamin, Cyclopentylamin, Piperidin, 4-Methylpiperidin, Cyclohexylamin und 1,1,3,3-Tetramethylbutylamin.
7. Verfahren nach Anspruch 1, wobei das wässrige Gemisch zudem Zeolith-Impfkristalle in einer so großen Menge umfasst, dass die Kristallisation geregelt und beschleunigt wird.
8. Verfahren nach Anspruch 1, wobei das Reaktionsgemisch, ausgedrückt als Molverhältnisse, umfasst:

M/YO ₂	0,01-0,50
OH-/YO ₂	0,01-0,60
H ₂ O/YO ₂	10-120
Q/YO ₂	0,02-1,00
YO ₂ /W ₂ O ₃	10-200
Z/YO ₂	0,05-1,00,

worin ist:

M ein Alkalimetall;
Y Silicium, Germanium oder beides;
Q die organische Templatverbindung;
Z die Aminkomponente; und
W Aluminium, Gallium, Eisen, Bor, Titan oder Gemische davon.

9. Verfahren nach Anspruch 8, wobei das Reaktionsgemisch, ausgedrückt als Molverhältnisse, umfasst:

M/YO ₂	0,10-0,20
OH-/YO ₂	0,10-0,30
H ₂ O/YO ₂	20-50
Q/YO ₂	0,02-0,10
YO ₂ /W ₂ O ₃	15-120
Z/YO ₂	0,20-0,40.

10. Verfahren nach Anspruch 4, wobei der Zeolith nach dem Brennen die in der nachstehenden Tabelle 2 angegebenen Röntgenbeugungslinien aufweist:

TABELLE 2

2θ	d/n	I/I ₀
3,4	25,5	17
7,19	12,30	100
8,04	11,00	55
10,06	8,78	63
14,35	6,17	40
16,06	5,51	17
22,77	3,90	38
23,80	3,74	20
26,08	3,417	65

11. Verfahren nach Anspruch 10, wobei die organische Templatverbindung Adamantanamin umfasst.
12. Verfahren nach Anspruch 11, wobei das Adamantanamin mindestens ein Adamantanamin aus der Gruppe 1-Adamantanamin oder 2-Adamantanamin umfasst.
13. Verfahren nach Anspruch 11, wobei die Aminkomponente Isobutylamin, 4-Methylpiperidin, Cyclopentylamin oder Piperidin umfasst.
14. Verfahren nach Anspruch 11, wobei die organische Templatverbindung Adamantanol umfasst.
15. Verfahren nach Anspruch 14, wobei das Adamantanol mindestens ein Adamantanol aus der Gruppe 1-Adamantanol und 2-Adamantanol umfasst.
16. Verfahren nach Anspruch 14, wobei die Aminkomponente Piperidin oder Isobutylamin umfasst.
17. Verfahren nach Anspruch 4, wobei der wie-synthetisierte Zeolith die Röntgenbeugungslinien der nachstehenden Tabelle A aufweist:

TABELLE A

2θ	d/n	I/I ₀
8,04	10,99	30,2
8,81	10,03	12,6
11,30	7,82	23,1
18,08	4,90	8,0
19,56	4,53	61,2
20,81	4,26	65,1
22,75	3,90	100,0
23,89	3,72	85,6
24,59	3,62	34,9
25,16	3,53	21,9
25,91	3,43	41,8
26,89	3,31	7,2
28,13	3,17	11,5
29,30	3,04	5,9
31,48	2,84	6,0

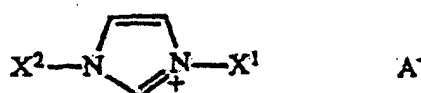
18. Verfahren nach Anspruch 17, wobei die organische Templatverbindung umfasst eine N,N'-disubstituierte Imidazolium-Verbindung oder ein N,N,N-Trialkyl-1,1,3,3-tetraalkylbutylammonium-Kation.
19. Verfahren nach Anspruch 18, wobei die Imidazoliumverbindung ein N,N'-Diisopropylimidazolium-Kation oder ein N-Methyl-N'-isopropylimidazolium-Kation ist.

20. Verfahren nach Anspruch 18, wobei das N,N,N-Trialkyl-1,1,3,3-tetraalkylbutylamonium-Kation ein N,N,N-Trime-
thyl-1,1,3,3-tetramethylbutylammonium-Kation ist.
21. Verfahren nach Anspruch 18, wobei die organische Templatverbindung eine N,N'-disubstituierte Imidazolium-ver-
bindung umfasst, und die Aminkomponente eine Verbindung umfasst, ausgewählt aus der Gruppe, bestehend aus
Isobutylamin, Methylamin, Ammoniumhydroxid, Butylamin, tert.-Butylamin, Dipropylamin, Isopropylamin und Cy-
clopentylamin.
22. Verfahren nach Anspruch 18, wobei die organische Templatverbindung ein N,N,N-Trialkyl-1,1,3,3-tetraalkylbutyl-
ammonium-Kation umfasst, und die Aminkomponente ausgewählt ist aus der Gruppe, bestehend aus Isobutyl-
amin, Cyclopentylamin, Isopropylamin und 1,1,3,3-Tetramethylbutylamin.
23. Verfahren nach Anspruch 4, wobei der Zeolith nach der Synthese die Röntgenbeugungslinien gemäß nachste-
hender Tabelle B aufweist:

TABELLE B

2 θ	d/n	I/I ₀
8,13	10,87	37,7
10,15	8,70	4,0
12,72	6,95	18,6
16,51	5,36	2,6
19,36	4,58	3,0
20,28	4,38	100,0
24,11	3,69	75,3
24,53	3,63	75,2
25,64	3,47	63,9

24. Verfahren nach Anspruch 23, wobei die organische Templatverbindung ein Piperidin-Derivat umfasst.
25. Verfahren nach Anspruch 24, wobei das Piperidin-Derivat 2,6-Dimethylpiperidin ist.
26. Verfahren nach Anspruch 24, wobei die Aminkomponente Isobutylamin, Cyclopentylamin oder Piperidin umfasst.
27. Verfahren nach Anspruch 23, wobei die organische Templatverbindung umfasst Imidazolsalze der Formel



wobei X¹ und X² unabhängig voneinander einen linearen Alkylrest mit 1 bis etwa 10 Kohlenstoffatomen darstellen,
und A⁻ ein Anion darstellt, das die Zeolithbildung nicht beeinträchtigt.

28. Verfahren nach Anspruch 4, wobei der Zeolith nach seiner Synthese die Röntgenbeugungslinien der nachstehen-
den Tabelle C aufweist:

TABELLE C

2 θ	d/n	I/I ₀
7,62	11,58	11,0
11,28	7,83	7,1
12,94	6,84	9,6
15,36	5,76	64,7
17,09	5,18	100,0

10

15

- 20

- 25

30

35

- 40



50

55

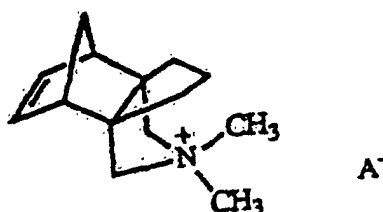
A⁻ ein Anion, das die Zeolithbildung nicht beeinträchtigt.

33. Verfahren nach Anspruch 32, wobei die organische Templatverbindung ein 1,6-N,N,N',N',N',N'-Hexamethylhexamethyldiammonium-Kation ist.
34. Verfahren nach Anspruch 32, wobei die Aminkomponente Isobutylamin oder Cyclopentylamin umfasst.
35. Verfahren nach Anspruch 31, wobei die organische Templatverbindung eine 4-Benzyl-N,N-dimethylpiperidinium-Verbindung ist.
36. Verfahren nach Anspruch 35, wobei die Aminkomponente Isobutylamin umfasst.
37. Verfahren nach Anspruch 4, wobei der Zeolith nach der Synthese die Röntgenbeugungslinien der nachstehenden Tabelle E aufweist:

TABELLE E

2 θ	d/n	I/I ₀
7,99	11,05	100,0
9,65	9,16	7,4
15,37	5,76	17,0
18,88	4,69	43,7
19,32	4,59	62,6
19,82	4,48	30,1
21,60	4,11	17,8
22,80	3,89	20,8
25,68	3,47	29,6
27,41	3,25	27,3
29,20	3,06	17,6

38. Verfahren nach Anspruch 37, wobei die organische Templatverbindung ausgewählt ist aus der Gruppe N-Ethyl-N-methyl-9-azoniabicyclo-[3.3.1]nonan-Kation und Verbindung der Formel:



wobei A⁻ ein Anion ist, das die Zeolithbildung nicht beeinträchtigt.

39. Verfahren nach Anspruch 38, wobei die Aminkomponente Isobutylamin, Cyclopentylamin oder Piperidin umfasst.
40. Verfahren nach Anspruch 4, wobei der wie-synthetisierte Zeolith die Röntgenbeugungslinien der nachstehenden Tabelle F aufweist:

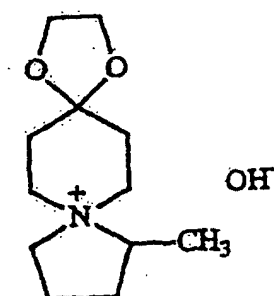
TABELLE F

2 θ	d/n	I/I ₀
7,43	11,05	24,4
8,70	10,15	9,5
18,87	4,70	15,6
19,90	4,46	6,9
20,75	4,28	100,0

TABELLE F (fortgesetzt)

2θ	d/n	I/I ₀
22,93	3,88	52,8
26,26	3,39	13,3
27,82	3,20	4,8
35,41	2,53	11,4

41. Verfahren nach Anspruch 40, wobei die organische Templatverbindung umfasst eine Verbindung der Formel:



42. Verfahren nach Anspruch 41, wobei die Aminkomponente Isobutylamin umfasst.

43. Zeolith, ausgewählt aus der Gruppe großporige Zeolithe, mittelporige Zeolithe mit eindimensionalen Kanälen und kleinporige Zeolithe, mit einer Molzusammensetzung nach der Synthese und im wasserfreien Zustand von (0,02 bis 2,0) Q: (0,02 bis 1,0) Z: (0,1 bis 2,0) M₂O:W₂O₃: (10 bis 200) YQ₂, worin ist:

M ein Alkalimetallkation;

W ausgewählt aus Aluminium, Gallium, Eisen, Bor, Titan, und Gemischen davon;

Y ausgewählt aus Silicium, Germanium, und Gemischen davon;

Z eine Aminkomponente, umfassend mindestens ein Amin, ausgewählt aus der Gruppe, bestehend aus Aminen mit 1 bis 8 Kohlenstoffatomen, Ammoniumhydroxid und Gemischen davon;

Q eine organische Templatverbindung, die in Gegenwart der Aminkomponente den Zeolith bilden kann,

wobei das Amin kleiner ist als die organische Templatverbindung und die organische Templatverbindung in einer Menge verwendet wird, die kleiner ist als man zur Kristallisation des Zeoliths in Abwesenheit der Aminkomponente benötigt.

44. Zeolith nach Anspruch 43, der nach dem Brennen die in der nachstehenden Tabelle 2 angegebenen Röntgenbeugungslinien aufweist:

TABELLE 2

2θ	d/n	I/I ₀
3,4	25,5	17
7,19	12,30	100
8,04	11,00	55
10,06	8,78	63
14,35	6,17	40
16,06	5,51	17
22,77	3,90	38
23,80	3,74	20
26,08	3,417	65

45. Zeolith nach Anspruch 43, der in der nach Synthese die Röntgenbeugungslinien der nachstehenden Tabelle A

aufweist:

TABELLE A

2 θ	d/n	I/I ₀
8,04	10,99	30,2
8,81	10,03	12,6
11,30	7,82	23,1
18,08	4,90	8,0
19,56	4,53	61,2
20,81	4,26	65,1
22,75	3,90	100,0
23,89	3,72	85,6
24,59	3,62	34,9
25,16	3,53	21,9
25,91	3,43	41,8
26,89	3,31	7,2
28,13	3,17	11,5
29,30	3,04	5,9
31,48	2,84	6,0

46. Zeolith nach Anspruch 43, der nach seiner Synthese die Röntgenbeugungslinien der nachstehenden Tabelle B aufweist:

TABELLE B

2 θ	d/n	I/I ₀
8,13	10,87	37,7
10,15	8,70	4,0
12,72	6,95	18,6
16,51	5,36	2,6
19,36	4,58	3,0
20,28	4,38	100,0
24,11	3,69	75,3
24,53	3,63	75,2
25,64	3,47	63,9

47. Zeolith nach Anspruch 43, der nach seiner Synthese die Röntgenbeugungslinien der nachstehenden Tabelle C aufweist:

TABELLE C

2 θ	d/n	I/I ₀
7,62	11,58	11,0
11,28	7,83	7,1
12,94	6,84	9,6
15,36	5,76	64,7
17,09	5,18	100,0
18,24	4,86	32,0
18,80	4,71	31,8
19,66	4,51	40,1
21,40	4,14	26,0
24,85	3,58	12,1
26,18	3,40	64,5
26,49	3,40	28,0

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TABELLE C (fortgesetzt)

2 θ	d/n	I/I ₀
26,85	3,32	28,6
28,14	3,17	13,7
29,75	3,00	13,0

48. Zeolith nach Anspruch 43, der nach seiner Synthese die Röntgenbeugungslinien der nachstehenden Tabelle D aufweist:

TABELLE D

2 θ	d/n	I/I ₀
7,92	11,15	48,3
8,70	10,15	21,5
9,06	9,75	6,0
12,87	6,87	2,3
19,04	4,65	39,7
20,53	4,32	100,0
22,15	4,01	61,8
23,26	3,82	31,8
23,94	3,71	20,0
25,97	3,43	9,3
26,52	3,36	9,4
27,29	3,26	34,8

49. Zeolith nach Anspruch 43, der nach seiner Synthese die Röntgenbeugungslinien der nachstehenden Tabelle E aufweist:

TABELLE E

2 θ	d/n	I/I ₀
7,99	11,05	100,0
9,65	9,16	7,4
15,37	5,76	17,0
18,88	4,69	43,7
19,32	4,59	62,6
19,82	4,48	30,1
21,60	4,11	17,8
22,80	3,89	20,8
25,68	3,47	29,6
27,41	3,25	27,3
29,20	3,06	17,6

50. Zeolith nach Anspruch 43, der nach seiner Synthese die Röntgenbeugungslinien der nachstehenden Tabelle F aufweist:

TABELLE F

2 θ	d/n	I/I ₀
7,43	11,05	24,4
8,70	10,15	9,5
18,87	4,70	15,6
19,90	4,46	6,9
20,75	4,28	100,0

TABELLE F (fortgesetzt)

2 θ	d/n	I/I ₀
22,93	3,88	52,8
26,26	3,39	13,3
27,82	3,20	4,8
35,41	2,53	11,4

Revendications

- Procédé pour la préparation d'une zéolite choisie dans le groupe consistant en des zéolites à grands pores, des zéolites à pores moyens ayant des canaux unidimensionnels et des zéolites à petits pores, ledit procédé comprenant les étapes consistant à :

A. former un mélange réactionnel aqueux comprenant (1) une source d'un oxyde choisi entre l'oxyde de silicium, l'oxyde de germanium et leurs mélanges ; (2) une source d'un oxyde choisi entre l'oxyde d'aluminium, l'oxyde de gallium, l'oxyde de fer, l'oxyde de bore, l'oxyde de titane et leurs mélanges ; (3) une source d'un métal alcalin ; (4) un constituant du type amine comprenant au moins une amine choisie dans le groupe consistant en : des amines contenant un à huit atomes de carbone ; l'hydroxyde d'ammonium ; et leurs mélanges, et (5) un composé organique servant de modèle permettant la formation de ladite zéolite en présence de ladite amine, ladite amine étant plus petite que ledit composé organique servant de modèle, et ledit agent organique servant de modèle étant utilisé en une quantité inférieure à celle requise pour la cristallisation de la zéolite en l'absence dudit constituant du type amine ; et

B. maintenir ledit mélange aqueux dans des conditions de cristallisation suffisantes jusqu'à la formation de cristaux.

- Procédé suivant la revendication 1, dans lequel la zéolite à grands pores a des canaux unidimensionnels.
- Procédé suivant la revendication 1, dans lequel la zéolite à grands pores a des canaux multidimensionnels.
- Procédé suivant la revendication 1, dans lequel le composé organique servant de modèle est choisi dans le groupe consistant en des ions ammonium quaternaire, des amines cycliques et des dérivés d'adamantyle polaires.
- Procédé suivant la revendication 1, dans lequel le constituant du type amine comprend une amine aliphatique, cycloaliphatique ou hétérocyclique, l'hydroxyde d'ammonium ou leurs mélanges.
- Procédé suivant la revendication 5, dans lequel le constituant du type amine comprend un composé choisi dans le groupe consistant en l'isobutylamine, la méthylamine, l'hydroxyde d'ammonium, la butylamine, la tertio-butylamine, la dipropylamine, l'isopropylamine, la cyclopentylamine, la pipéridine, la 4-méthylpipéridine, la cyclohexylamine et la 1,1,3,3-tétraméthylbutylamine.
- Procédé suivant la revendication 1, dans lequel le mélange aqueux comprend en outre des germes de cristaux de zéolite en une quantité suffisante pour diriger et accélérer la cristallisation.
- Procédé suivant la revendication 1, dans lequel le mélange réactionnel comprend les constituants suivants en termes de rapports molaires :

M/YO ₂	0.01-0.50
OH ⁻ /YO ₂	0.01-0.60
H ₂ O/YO ₂	10-120
Q/YO ₂	0.02-1.00
YO ₂ /W ₂ O ₃	10-200
Z/YO ₂	0.05-1.00

dans lesquels M représente un métal alcalin, Y représente le silicium, le germanium ou ses deux éléments ; Q représente le composé organique servant de modèle, Z représente le constituant du type amine ; et W représente

l'aluminium, le gallium, le fer, le bore, le titane ou leurs mélanges.

9. Procédé suivant la revendication 8, dans lequel le mélange réactionnel comprend les ingrédients suivants en termes de, rapports molaires :

M/YO ₂	0.10-0.20
OH/YO ₂	0.10-0.30
H ₂ O/YO ₂	20-50
Q/YO ₂	0.02-0.10
YO ₂ /W ₂ O ₃	15-120
Z/YO ₂	0.20-0.40

10. Procédé suivant la revendication 4, dans lequel la zéolite a, après calcination, le diagramme de diffraction des rayons X figurant sur le tableau 2 suivant :

TABLEAU 2

2 θ	d/n	I/I ₀
3.4	25.5	17
7.19	12.30	100
8.04	11.00	55
10.06	8.78	63
14.35	6.17	40
16.06	5.51	17
22.77	3.90	38
23.80	3.74	20
26.08	3.417	65

11. Procédé suivant la revendication 10, dans lequel le composé organique servant de modèle comprend l'adamantanamine.

12. Procédé suivant la revendication 11, dans lequel l'adamantanamine comprend au moins une adamantanamine du groupe comprenant la 1-adamantanamine ou la 2-adamantanamine.

13. Procédé suivant la revendication 11, dans lequel le constituant du type amine comprend l'isobutylamine, la 4-méthylpipéridine, la cyclopentylamine ou la pipéridine.

14. Procédé suivant la revendication 11, dans lequel le composé organique servant de modèle comprend l'adamantanol.

15. Procédé suivant la revendication 14, dans lequel l'adamantanol comprend au moins un adamantanol du groupe comprenant le 1-adamantanol et le 2-adamantanol.

16. Procédé suivant la revendication 14, dans lequel le constituant du type amine comprend la pipéridine ou l'isobutylamine.

17. Procédé suivant la revendication 4, dans lequel la zéolite, telle qu'obtenue par synthèse, a le diagramme de diffraction des rayons X figurant sur le tableau A suivant :

TABLEAU A

2 θ	d/n	I/I ₀
8.04	10.99	30.2
8.81	10.03	12.6
11.30	7.82	23.1
18.08	4.90	8.0

TABLEAU A (suite)

2 θ	d/n	I/I ₀
19.56	4.53	61.2
20.81	4.26	65.1
22.75	3.90	100.0
23.89	3.72	85.6
24.59	3.62	34.9
25.16	3.53	21.9
25.91	3.43	41.8
26.89	3.31	7.2
28.13	3.17	11.5
29.30	3.04	5.9
31.48	2.84	6.0

18. Procédé suivant la revendication 17, dans lequel le composé organique servant de modèle comprend un composé d'imidazolium N,N'-disubstitué ou un cation N,N,N-trialkyl-1,1,3,3-tétra-alkylbutylammonium.

19. Procédé suivant la revendication 18, dans lequel le composé d'imidazolium est un cation N,N'-diisopropylimidazolium ou un cation N-méthyl-N'-isopropylimidazolium.

20. Procédé suivant la revendication 18, dans lequel le cation N,N,N-trialkyl-1,1,3,3-tétra-alkylbutylammonium est un cation N,N,N-triméthyl-1,1,3,3-tétraméthylbutylammonium.

21. Procédé suivant la revendication 18, dans lequel le composé organique servant de modèle comprend un composé d'imidazolium N,N'-disubstitué et le constituant du type amine comprend un composé choisi dans le groupe consistant en l'isobutylamine, la méthylamine, l'hydroxyde d'ammonium, le butylamine, la tertio-butylamine, la dipropylamine, l'isopropylamine et la cyclopentylamine.

22. Procédé suivant la revendication 18, dans lequel le composé organique servant de modèle comprend un cation N,N,N-trialkyl-1,1,3,3-tétra-alkylbutylammonium et le constituant du type amine est choisi dans le groupe consistant en l'isobutylamine, la cyclopentylamine, l'isopropylamine et la 1,1,3,3-tétraméthylbutylamine.

23. Procédé suivant la revendication 4, dans lequel la zéolite a, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau B suivant :

TABLEAU B

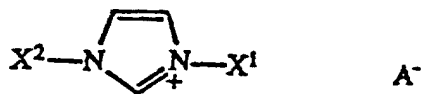
2 θ	d/n	I/I ₀
8.13	10.87	37.7
10.15	8.70	4.0
12.72	6.95	18.6
16.51	5.36	2.6
19.36	4.58	3.0
20.28	4.38	100.0
24.11	3.69	75.3
24.53	3.63	75.2
25.64	3.47	63.9

24. Procédé suivant la revendication 23, dans lequel le composé organique servant de modèle comprend un dérivé de pipéridine.

25. Procédé suivant la revendication 24, dans lequel le dérivé, de pipéridine est la 2,6-diméthylpipéridine.

26. Procédé suivant la revendication 24, dans lequel le constituant du type amine comprend l'isobutylamine, la cyclopentylamine ou la pipéridine.

27. Procédé suivant la revendication 23, dans lequel le composé organique servant de modèle comprend des sels d'imidazole de formule



dans laquelle X^1 et X^2 représentent, indépendamment, un groupe alkyle linéaire contenant 1 à environ 10 atomes de carbone, A^- représente un anion qui n'est pas néfaste pour la formation de la zéolite.

28. Procédé suivant la revendication 4, dans lequel la zéolite a, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau C suivant :

TABLEAU C

2 θ	d/n	I/I ₀
7.62	11.58	11.0
11.28	7.83	7.1
12.94	6.84	9.6
15.36	5.76	64.7
17.09	5.18	100.0
18.24	4.86	32.0
18.80	4.71	31.8
19.66	4.51	40.1
21.40	4.14	26.0
24.85	3.58	12.1
26.18	3.40	64.5
26.49	3.40	28.0
26.85	3.32	28.6
28.14	3.17	13.7
29.75	3.00	13.0

29. Procédé suivant la revendication 28, dans lequel le composé organique servant de modèle est choisi dans le groupe consistant en les cations N,N-diméthyltropinium et N,N-diméthyl-3-azonium-bicyclo-[3.2.2] -nonane.

30. Procédé suivant la revendication 29, dans lequel le constituant du type amine comprend l'isobutylamine, la cyclopentylamine ou la pipéridine.

31. Procédé suivant la revendication 4, dans lequel la zéolite a, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau D suivant :

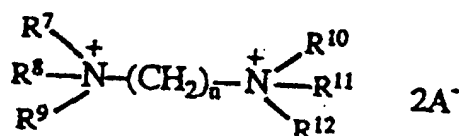
TABLEAU D

2 θ	d/n	I/I ₀
7.92	11.15	48.3
8.70	10.15	21.5
9.06	9.75	6.0
12.87	6.87	2.3
19.04	4.65	39.7
20.53	4.32	100.0
22.15	4.01	61.8
23.26	3.82	31.8
23.94	3.71	20.0

TABLEAU D (suite)

2 θ	d/n	I/I ₀
25.97	3.43	9.3
26.52	3.36	9.4
27.29	3.26	34.8

32. Procédé suivant la revendication 31, dans lequel le composé organique servant de modèle comprend des dérivés alkylés d'une polyméthylènediamine répondant à la formule :



dans laquelle n est compris dans l'intervalle de 3 à 12, R⁷ à R¹², qui peuvent être identiques ou différents, représentent l'hydrogène, des groupes alkyle ou hydroxy-alkyle contenant 1 à 8 atomes de carbone, jusqu'à cinq des groupes R⁷ à R¹² pouvant représenter l'hydrogène, et A⁻ représente un anion qui n'est pas néfaste pour la formation de la zéolite.

33. Procédé suivant la revendication 32, dans lequel le composé organique servant de modèle comprend un cation 1,6-N,N,N,N',N',N'-hexaméthyl-hexaméthylène-diammonium.

34. Procédé suivant la revendication 32, dans lequel le constituant du type amine comprend l'isobutylamine ou la cyclopentylamine.

35. Procédé suivant la revendication 31, dans lequel le composé organique servant de modèle est un composé de 4-benzyl-N,N-diméthylpipéridinium.

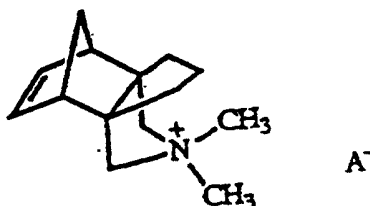
36. Procédé suivant la revendication 35, dans lequel le constituant du type amine comprend l'isobutylamine.

37. Procédé suivant la revendication 4, dans lequel la zéolite a, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau E suivant :

TABLEAU E

2θ	d/n	I/I ₀
7.99	11.05	100.0
9.65	9.16	7.4
15.37	5.76	17.0
18.88	4.69	43.7
19.32	4.59	62.6
19.82	4.48	30.1
21.60	4.11	17.8
22.80	3.89	20.8
25.68	3.47	29.6
27.41	3.25	27.3
29.20	3.06	17.6

38. Procédé suivant la revendication 37, dans lequel le composé organique servant de modèle est choisi dans le groupe consistant en un cation N-éthyl-N-méthyl-9-azonia-bicyclo[3.3.1]nonane et un composé répondant à la formule suivante :



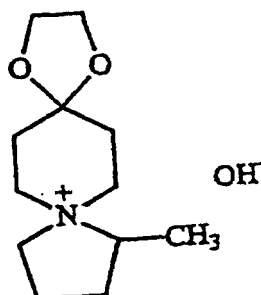
dans laquelle A⁻ représente un anion qui n'est pas néfaste à la formation de la zéolite.

39. Procédé suivant la revendication 38, dans lequel le constituant du type amine comprend l'isobutylamine, la cyclopentylamine ou la pipéridine.

40. Procédé suivant la revendication 4, dans lequel la zéolite, telle qu'obtenue par synthèse, a le diagramme de diffraction des rayons X figurant sur le tableau F suivant :

2 θ	d/n	I/I ₀
7.43	11.05	24.4
8.70	10.15	9.5
18.87	4.70	15.6
15.90	4.46	6.9
20.75	4.28	100.0
22.93	3.88	52.8
26.26	3.39	13.3
27.82	3.20	4.8
35.41	2.53	11.4

41. Procédé suivant la revendication 40, dans lequel le composé organique servant de modèle comprend un composé répondant à la formule suivante :



42. Procédé suivant la revendication 41, dans lequel le constituant du type amine comprend l'isobutylamine.

43. Zéolite choisie dans le groupe consistant en des zéolites à grands pores, des zéolites à pores moyens ayant des canaux unidimensionnels et des zéolites à petits pores, ayant la composition molaire suivante, telle qu'obtenue par synthèse et à l'état anhydre de : (0,02 à 2,0) Q : (0,02 à 1,0) Z : (0,1 à 2,0) M₂O:W₂O₃ : (10 à 200) YO₂, dans laquelle M représente un cation de métal alcalin ; W est choisi entre l'aluminium, le gallium, le fer, le bore, le titane et leurs mélanges ; Y est choisi entre le silicium, le germanium et leurs mélanges ; Z représente un constituant du type amine comprenant au moins une amine choisie dans le groupe consistant en : des amines contenant 1 à 8 atomes de carbone ; l'hydroxyde d'ammonium et leurs mélanges ; Q représente un composé organique servant de modèle permettant la formation de la zéolite en présence dudit constituant du type amine, ladite amine étant plus petite que le composé organique servant de modèle, et ledit agent organique servant de modèle étant utilisé en une quantité inférieure à la quantité requise pour la cristallisation de la zéolite en l'absence dudit constituant

du type amine.

44. Zéolite suivant la revendication 43, ayant, après calcination, le diagramme de diffraction des rayons X figurant sur le tableau 2 suivant :

TABLEAU 2

2 θ	d/n	I/I ₀
3.4	25.5	17
7.19	12.30	100
8.04	11.00	55
10.06	8.78	63
14.35	6.17	40
16.06	5.51	17
22.77	3.90	38
23.80	3.74	20
26.08	3.417	65

45. Zéolite suivant la revendication 43, ayant, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau A suivant :

TABLEAU A

2 θ	d/n	I/I ₀
8.04	10.99	30.2
8.81	10.03	12.6
11.30	7.82	23.1
18.08	4.90	8.0
19.56	4.53	61.2
20.81	4.26	65.1
22.75	3.90	100.0
23.89	3.72	85.6
24.59	3.62	34.9
25.16	3.53	21.9
25.91	3.43	41.8
26.89	3.31	7.2
28.13	3.17	11.5
29.30	3.04	5.9
31.48	2.84	6.0

46. Zéolite suivant la revendication 43, ayant, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau B suivant :

TABLEAU B

2 θ	d/n	I/I ₀
8.13	10.87	37.7
10.15	8.70	4.0
12.72	6.95	18.6
16.51	5.36	2.6
19.36	4.58	3.0
20.28	4.38	100.0
24.11	3.69	75.3
24.53	3.63	75.2
25.64	3.47	63.9

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47. Zéolite suivant la revendication 43, ayant, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau C suivant :

TABLEAU C

2 θ	d/n	I/I ₀
7.62	11.58	11.0
11.28	7.83	7.1
12.94	6.84	9.6
15.36	5.76	64.7
17.09	5.18	100.0
18.24	4.86	32.0
18.80	4.71	31.8
19.66	4.51	40.1
21.40	4.14	26.0
24.85	3.58	12.1
26.18	3.40	64.5
26.49	3.40	28.0
26.85	3.32	28.6
28.14	3.17	13.7
29.75	3.00	13.0

48. Zéolite suivant la revendication 43, ayant, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau D suivant :

TABLEAU D

2 θ	d/n	I/I ₀
7.92	11.15	48.3
8.70	10.15	21.5
9.06	9.75	6.0
12.87	6.87	2.3
19.04	4.65	39.7
20.53	4.32	100.0
22.15	4.01	61.8
23.26	3.82	31.8
23.94	3.71	20.0
25.97	3.43	9.3
26.52	3.36	9.4
27.29	3.26	34.8

49. Zéolite suivant la revendication 43, ayant, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau E suivant :

TABLEAU E

2 θ	d/n	I/I ₀
7.99	11.05	100.0
9.65	9.16	7.4
15.37	5.76	17.0
18.88	4.69	43.7
19.32	4.59	62.6
19.82	4.48	30.1
21.60	4.11	17.8
22.80	3.89	20.8

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TABLEAU E (suite)

2 θ	d/n	I/I ₀
25.68	3.47	29.6
27.41	3.25	27.3
29.20	3.06	17.6

50. Zéolite suivant la revendication 43, ayant, sous la forme telle qu'obtenue par synthèse, le diagramme de diffraction des rayons X figurant sur le tableau F suivant :

TABLEAU F

2 θ	d	I/I ₀ x 100
7.43	11.05	24.4
8.70	10.15	9.5
18.87	4.70	15.6
19.90	4.46	6.9
20.75	4.28	100.0
22.93	3.88	52.8
26.26	3.39	13.3
27.82	3.20	4.8
35.41	2.53	11.4